Sara Sobral Babo

Mestre em Conservação e Restauro

From industry to artworks by Lourdes Castro and Ângelo de Sousa: conservation studies on cast acrylic sheet

Dissertação para obtenção do Grau de Doutor em
Conservação e Restauro, especialidade em Ciências da Conservação

Orientador: Doutora Joana Lia Antunes Ferreira Marçal Grilo, Professora Auxiliar, Faculdade de Ciências e Tecnologia da Universidade NOVA de Lisboa

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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[Verso da Capa]

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Dedicated to the memory of Augusta Lima

Acknowledgements

This PhD was funded by Fundação para a Ciência e Tecnologia - Ministério da Educação e Ciência (FCT-MEC), through the doctoral grant SFRH/BD/52318/2013.

Because it would not have been possible to accomplish this work alone, I would like to thank all those who helped me along this path.

First, I thank my supervisor, Professor Joana Lia Ferreira, for the trust she placed in me to carry out this project. Her encouragement during the final stage of writing the thesis was crucial to complete this work. I also thank my co-supervisors, Professor Maria João Melo and Professor Ana Maria Ramos, for their knowledge and support along this journey. Thank you also to the external CAT members, Professor Teresa Cidade and Tim Bechthold.

I am also grateful to Lourdes Castro for her kindness and generosity in offering some of her acrylic samples for this study. And to Miguel de Sousa, Ângelo de Sousa's heir, for hosting me in Porto and letting me study Ângelo de Sousa's extraordinary collection. Researching part of the work of these two artists was a real privilege.

My gratitude also goes to the directors and staff of the surveyed museums and collections, for giving me access to all the works that I was able to examine. I would like to thank Isabel Corte-Real and Maria Manuel Conceição (Colecção Caixa Geral de Depósitos); Ana Vasconcelos, Patrícia Nóbrega and Carlos Gonçalinho (Centro de Arte Moderna – Fundação Calouste Gulbenkian); Adelaide Ginga (Museu Nacional de Arte Contemporânea do Chiado); Pedro Lapa and Francisca Sousa (Museu Colecção Berardo); Rui Brito and Ana Paula Migalhada (Centro de Arte Manuel de Brito); Filipe Duarte (Serralves); and Patrícia Machado (Museu de Arte Contemporânea de Elvas).

I also thank Carlos Carvalheira, Sónia Apkan, Maria Augusta Apkan and Manuel Freitas for sharing with me their memories and knowledge about the production of acrylic sheet in the companies where they have worked. To Dr Elvira Callapez, I thank the initial guidance in research about plastics production history in Portugal. And to Professor Bernardo Pinto de Almeida I thank the amiability for sharing his thoughs about Ângelo de Sousa’s work.

I am grateful to Dr Marisa Pamplona and Dr Anna Micheluz, from the Deutsches Museum, for how they welcomed me in Munich and for carrying out the TD-GC/MS analyses. Thank you also to Dr Luís Ferreira and Dr Maria Helena Casimiro for their kindness in receiving me at C2TN and their guidance during the thermal analyses.

I am also grateful to Professor Rui Silva (DCM and CENIMAT|I3N) for the access to the Vickers hardness testing machine; to Professor César Laia, Dr Andreia Ruivo and Dr Sandra Gago for their assistance in the use of spectrophotometers; and to Professor Fernando Pina and Professor Jorge Parola for the support in the synthesis of plumbonacrite. My thanks also to the FCT FabLab, where I cut hundreds of PMMA samples, especially to Filipe Silvestre the assistance provided. Many thanks to Nuno Costa, from the Analysis Laboratory LAQV REQUIMTE, for performing the SEC analysis (when I had stopped believing that it would ever be possible) and to Dr Vítor Rosa for distilling the several litres of THF necessary for this technique. They were both essential for the conclusion of this work.

My gratitude also to my department, DCR, in particular to Professors Leslie Carlyle and Rita Macedo for their support and contributions to this thesis; to Ana Maria Martins, for always managing to deal with boring things with a smile; and to Vanessa Otero, for her friendship and for always helping me in the most diverse ways. I would also like to thank all my PhD/office colleagues, in particular: Eva Angelin, my out-of-hours lab mate in the plumbonacrite saga, for all the strength she transmitted to me throughout this project, Joana Devesa for all her support and sharing as a paintings conservator, Paula Nabais for her valuable advices, Alexandra Rodrigues for the shut-up-and-write sessions, and especially Susana França de Sá and Joana Silva for the productive discussions and support in writing the thesis. Thank you both very much!

I also thank my dear friends, especially to Maria João Pacheco and to the "turminha" group, with whom I started this journey in studying conservation, Augusta Lima, Madalena Costa, Maria Bastião, Maria João Revez, Marta Raposo, and Miguel Silva.

Finally, I thank João Paulo and my Parents, for their love and for keeping me fed and happy.

Abstract

Acrylic sheet, a plastic based on poly(methyl methacrylate) (PMMA), became popular within artists during the 1960s, when it was also used by two major Portuguese artists, Lourdes Castro (*1930) and Ângelo de Sousa (1938–2011). Taking as a starting point their work with this material, this thesis seeks to expand knowledge about the use of PMMA in art, its stability, and preservation. Therefore, a survey on artworks containing PMMA in Portuguese collections, as well as research on the history of production of this material in Portugal, was conducted in parallel with a material study of acrylic sheets used by those artists, and sheets produced by two Portuguese companies from which production processes were investigated and compared. This study included an artificial ageing experiment conducted in a solarbox ($\lambda > 300$ nm) for 8000 h, besides the characterization of the samples combining optical microscopy, colorimetry, gravimetry, micro-indentation, Raman, infrared and ultraviolet-visible spectroscopies, size exclusion chromatography, thermogravimetry, and thermo-desorption-gas chromatography/mass spectrometry.

For the survey, 137 artworks from 8 Portuguese art collections were considered, providing an overview of the use of this material by artists and of its condition. Artworks surveyed included paintings, sculptures, objects/reliefs, photography, installations and artist books. From the 69 authors, 48 were Portuguese and have used PMMA from the 1960s to nowadays. Most of the artworks were in good or fair condition, and the main problems observed were dust and dirt deposits, abrasion, and scratches.

This research showed that PMMA sheet was produced in Portugal between 1955 and 2009. At least four companies operated during the 1960s and all except one, produced nacreous PMMA sheets from recovered monomer obtained by depolymerization of acrylic residues.

The material used by Ângelo de Sousa falls within this category. Concerns about the quality of these sheets led to a comparative study between PMMA samples of different typologies and origins. Results revealed a connection between particular aspects of the production technique (polymerization conditions, organic additives, and origin of monomer) with the properties (molecular weight, hardness, thermal stability) and long-term behaviour of acrylic sheets. The pigment responsible for the nacreous effect in Ângelo de Sousa's acrylic sheets showed signs of instability during the

photodegradation experience, and was identified as plumbonacrite, $Pb_5(CO_3)_3O(OH)_2$, by Raman microspectroscopy.

Cleaning and polishing treatments (as the ones used by Lourdes Castro for finishing her artworks) were also investigated in terms of immediate and long-term effects in the samples that had presented higher and lower photostability in the artificial ageing experiment. Treatments' impact seems to be dependent of the particularities of the acrylic sheet under testing.

This research highlights that not all acrylic sheets present the same stability, which may be relevant for establishing new monitoring plans and preventive conservation measures, as well as to consider when testing interventive treatments in this material.

Key words: poly(methyl methacrylate); Lourdes Castro; Ângelo de Sousa; photodegradation; plumbonacrite; plastic conservation.

Resumo

A chapa acrílica, um plástico à base de poli(metacrilato de metilo) (PMMA), tornou-se popular entre os artistas durante a década de 1960, período em que foi também utilizada por dois grandes artistas portugueses, Lourdes Castro (*1930) e Ângelo de Sousa (1938-2011). Tendo como ponto de partida o seu trabalho com este material, esta tese procura contribuir para o conhecimento sobre a utilização do PMMA na arte, sobre a sua estabilidade e sobre a sua preservação. Assim, em paralelo com um levantamento de obras de arte contendo PMMA em colecções portuguesas, bem como uma investigação sobre a história da produção deste material em Portugal, foi realizado um estudo material comparativo, que abrangeu tanto chapas acrílicas utilizadas pelos dois artistas em estudo, como chapas produzidas por duas empresas portuguesas das quais os processos de produção foram investigados. Este estudo incluiu uma experiência de envelhecimento artificial realizada numa solarbox ($\lambda > 300$ nm) durante 8000 h, e a caracterização das amostras combinando microscopia óptica, colorimetria, gravimetria, microindentação, espectroscopias Raman, de infravermelho e de ultravioleta-visível, cromatografia de exclusão molecular, termogravimetria, e espectrometria de massa por cromatografia em fase gasosa.

Para o levantamento, foram consideradas 137 obras de arte de 8 colecções nacionais, permitindo obter uma visão geral acerca da forma como os artistas utilizaram este material, mas também do seu estado de conservação. As obras de arte consideradas incluem pinturas, esculturas, objectos/relevos, fotografia, instalações e livros de artista. Dos 69 autores, 48 são portugueses e utilizaram PMMA desde os anos 60 até aos dias de hoje. A maioria das obras de arte estava em boas condições ou razoáveis; os principais problemas observados foram depósitos de pó e sujidade, abrasão e riscos.

Esta investigação mostrou que chapa de PMMA foi produzida em Portugal entre 1955 e 2009. Pelo menos quatro empresas operaram durante a década de 1960 e todas, excepto uma, produziram chapas de PMMA nacaradas a partir de monómero recuperado obtido por despolimerização de resíduos acrílicos.

O material utilizado por Ângelo de Sousa enquadra-se nesta categoria. Preocupações sobre a qualidade destas chapas levaram a um estudo comparativo entre amostras de PMMA de diferentes tipologias e origens. Os resultados revelaram uma relação entre aspectos particulares da técnica de produção (condições de polimerização, aditivos orgânicos, e origem do monómero) com as propriedades (ex. peso molecular, dureza, estabilidade térmica) e comportamento a longo prazo das chapas acrílicas. O

pigmento responsável pelo efeito nacarado nas chapas acrílicas de Ângelo de Sousa mostrou sinais de instabilidade durante a experiência da fotodegradação, e foi identificado como plumbonacrite, $Pb_5(CO_3)_3O(OH)_2$, através de microespectroscopia Raman.

Tratamentos de limpeza e polimento (como os utilizados por Lourdes Castro para acabamento das suas obras) foram também investigados em termos de efeitos imediatos e a longo prazo nas amostras que tinham apresentado maior e menor foto-estabilidade na experiência de envelhecimento artificial. O impacto dos tratamentos parece estar dependente das particularidades da chapa acrílica em teste.

Esta investigação salienta que nem todas as chapas de acrílico apresentam a mesma estabilidade, o que pode ser relevante para estabelecer novos planos de monitorização e medidas de conservação preventiva, bem como para intervenções de conservação e restauro neste material.

Key words: poli(metacrilato de metilo); Lourdes Castro; Ângelo de Sousa; fotodegradação; plumbonacrite; conservação de plásticos.

Table of Contents

List of Tables

List of Figures

Symbols and notations

Δ	variation
ΔE	total colour variation
λ	wavelength
μ	micro
$\bar{x}$	average
σ	standard deviation
ATR	attenuated total reflectance
CAMB	Centro de Arte Manuel de Brito
CAM-FCG	Centro de Arte Moderna – Fundação Calouste Gulbenkian
CGD	Caixa Geral de Depósitos
DE	Germany
DCR	Department of Conservation and Restoration
DGSI	Direcção Geral dos Serviços Industriais
FCT	Faculdade de Ciências e Tecnologia
FCG	Fundação Calouste Gulbenkian
FR	France
FTIR	Fourier Transform Infrared Spectroscopy
MACE	Museu de Arte Contemporânea de Elvas
MCB	Museu Coleção Berardo
MNAC	Museu Nacional de Arte Contemporânea Museu do Chiado
M_n	number-average molecular weight
M_w	weight-average molecular weight
$Đ_M$	molecular-weight dispersity
PMMA	poly(methyl methacrylate)
PVC	poly(vinyl chloride)
SEM-EDS	scanning electron microscopy – energy dispersive X-ray spectroscopy
t	time
T	temperature
T_g	glass transition temperature
TGA	thermogravimetric analysis
UNL	Universidade Nova de Lisboa
UK	United Kingdom
USA	United States of America
UV-Vis	Ultra-Violet and Visible

1 General Introduction

1.1 Backgroung of the research project

Plastics are an important part of our heritage. Despite the bad reputation gained due to their impact on wildlife, it is unquestionable that the discovery and development of plastics is one of the main chemical and technological achievements of the last century. The possibilities created by these new materials have enabled innovation in fields so diverse such as aviation, medicine, food packageing, or information storage, which in turn have revolutionized the way we live. As Susan Freinkel wrote, "plastic is the defining medium of life today – touching every aspect of our lives: our homes, our workplaces, the ways we dress, eat, play, and transport ourselves." (Freinkel 2017, 165). The transformation resulting from the introduction of plastics during the 20th century is so profound that it may be considered a marker for a new historical era, the "Plastic Age" (Thompson et al. 2009; Madden 2017), as prophesized by some authors during the early-1940s (Meikle 1995, 64-69). Furthermore, this designation is supported by the amount of plastic produced worldwide, which has surpassed the one of steel worldwide around 1980 (Morgan 1991; Shashoua 2008, 1) and has continued to grow (PlasticsEurope 2020). The history of plastics development, and its significance in our society, is beyond the scope of this thesis and it has been well covered by other authors (e.g. Sparke 1990; Mossman and Morris 1994; Meikle 1995; Fenichell 1997; Mossman 1997; Waentig 2008). Given the relevance of plastics in the technological, cultural, and domestic fields, it is not surprising that they have increasingly become an important part of museum collections. Plastics are found not only in art, design and historic

technological collections, but also in fashion and ethnographic collections, or in image and sound archives (e.g. Quye and Williamson 1999; Grattan 1993).

The presence of plastics in museums resulted in new conservation challenges and, consequently, on the development of a new conservation field dedicated to the research and preservation of plastics. This area has had an incredible evolution since its beginning in the early 1990s, and knowledge based on research has evolved from the understanding of degradation pathways to the development of cutting-edge treatments in more recent years (Madden and Learner 2014; Shashoua 2016). Even so, given the diversity of plastics (including the diversity of formulations and processing techniques for a given polymer) and our short experience with them (if we compare with traditional materials), there is still much to learn in this field, and research on specific plastics stabilities and conservation procedures is fundamental.

This thesis is focused on the conservation of a specific plastic, poly(methyl methacrylate) (PMMA), produced in the form of acrylic sheet and commonly known by the commercial names Plexiglas® or Perspex®. In conservation, PMMA is generally considered a stable plastic (Melo et al 1999; Waentig 2008, 274; Ferreira et al. 2011) and most of the problems identified in acrylic artefacts are related with mechanical damages externally induced to them (Lorne 1999; Kenenghan et al. 2012). But are all acrylic sheets identically stable? So far, very little attention has been given to the possible influence of different formulations, industrial production methods, and artists' techniques on the long-term stability of acrylic sheet used in artworks, or its response to conservation treatments.

Even though the polymer is the defining element of a plastic, plastics are not pure compounds. They are modified with fillers, colorants and other additives that make material processing easier, enhance their physical properties, and improve the environmental stability and long-term performance of the final product[1] (Bart 2005). However, as Scott Williams noted already in 1991 (Williams 1993), these complex mixtures of polymers and additives are designed to be effective during the *service lifetime* of the plastic objects, but might not necessarily remain so throughout their *museum lifetime*, which is expected to be much longer. Alterations induced by the presence of colourants or additives in the ageing of stable polymers were researched by several authors (e.g. Ferreira et al. 2010; Toja et al. 2012; Pintus et al. 2013). In what concerns PMMA artefacts specifically, the influence of additives in their museum lifetime has not been closely examined in the literature.

[1] Additives for plastics have been the subject of several comprehensive publications (e.g. Pritchard 1998; Flick 2001; Bart 2005; and Bauer 2018).

Another aspect that can have a profound influence on the properties of the material is the processing technology. The same polymer may be transformed into films, sheets, fibres, or moulded objects that will present obvious different characteristics. If we go one step further, even the same typology of material may have different properties depending on the process used to produce it. This is the case of acrylic sheets, which can be cast or extruded. It is known that due to their fabrication process, extruded sheets have molecular weights around 10^5 and the polymer chains are aligned in the extrusion direction, while cast sheets have higher molecular weights (10^6) and no directional preference of chain alignment. As result, extruded PMMA sheets have lower mechanical resistance in the direction perpendicular to chain orientation, lower heat and chemicals resistance, and lower surface quality and optical properties (Stickler and Rhein 1992; Sale 1993). However, as a rule, the knowledge conservators have about a material stops at this point, and differences caused by the way the same process is performed (such as different procedures for manufacturing cast acrylic sheets) are normally not considered.

This thesis is aimed at exploring further these aspects and their implications for the preservation of acrylic artworks. Because PMMA is used in so many different fields (e.g. medicine, solar energy, civil engineering, data storage) the amount of published scientific literature about this material is massive. The majority of these studies is very specific and hard to correlate with artworks. For the conservation field, studies that integrate part of this dispersed knowledge and that include long-term ageing experiences under conditions at least comparable with the reality of objects in museums are missing. But before discussing further the scope of this thesis, some background information about PMMA and its use in artworks is presented in the next subsections.

1.1.1 A brief introduction to PMMA and acrylic sheets

Poly(methyl methacrylate)[2] or PMMA is synthesized by chain (free radical) polymerization of the methyl methacrylate (MMA) monomer (Figure 1.1). The pendent side groups in the structure prevent the packing of the chains in a crystalline way and from rotating freely around the C-C bonds, which makes PMMA an amorphous thermoplastic (Ali et al. 2015). They also restrict chain flexibility, being responsible for the high glass transition temperature (Tg) of the polymer around 104°C, which makes PMMA a rigid transparent plastic at normal ambient conditions of use (Brydson 1989, 405).

[2] IUPAC name: poly(methyl 2-methylpropenoate) or poly[1-(methoxy carbonyl)-1-methyl ethylene], from the hydrocarbon standpoint and from the ester standpoint, respectively.

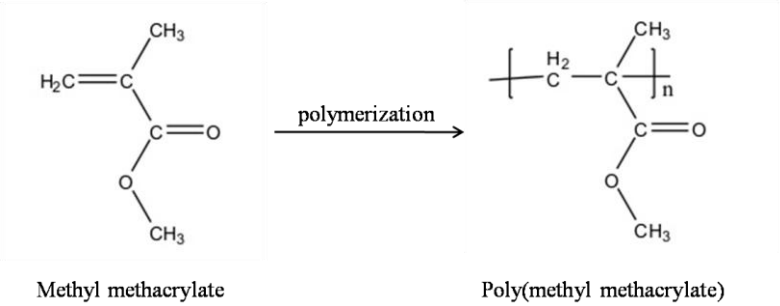


Figure 1.1: Chemical structures of the monomer MMA and the polymer PMMA.

Because PMMA is soluble in its own monomer, the chain polymerization can be made in bulk, slowly and with very few impurities, resulting in a polymer with outstanding optical properties (Painter and Coleman 2009, 80), which was a fundamental aspect in its development as a substitute of glass.

Research into the acrylic family started in the 2nd half of the 19thcentury. In 1873, Caspary and Tollens prepared for the first time various esters of acrylic acid; then, around 1880, Kahlbaum was able to polymerize methyl acrylate and Fittig found that methacrylic acid and some of its derivates also polymerized (Brydson 1999, 398). In 1901 Otto Rohm presented his PhD dissertation on "acrylic acid, its derivates, and their polymers" but it was only after World War I that the research on acrylic polymers continued. In 1918, with the raising interest by the automotive industry in finding a substitute for cellulose acetate in safety glass, Rohm employed the chemist Walter Bauer to continue his research on acrylic resins. His company, Röhm und Haas[3], introduced in 1928 the first commercial acrylic products (Cholod and Miller 1992, 288); these were soft gummy products, named Acryloid and Plexigum (Brydson 1999, 399). Imperial Chemical Industries, in England, were also researching these polymers and, in the early 1930s, both groups discovered independently the rigid, transparent and thermoformable plastic PMMA. However, only in 1932, after John Crawford has discovered a commercially viable manufacturing process to produce the monomer, it was possible to produce acrylic sheets on an industrial scale (PHS 2015). PMMA sheet was first produced commercially in 1934, both in Germany by Röhm und Haas, and in England by Imperial Chemical Industries Ltd (ICI). DuPont, in the United States of America, started to produce PMMA two years later, after making an agreement with ICI (Michel n.d.; Waentig 2008, 272). The material was commercialized under different

[3] Röhm und Haas was founded as a partnership by Otto Rohm and the businessman Otto Haas in 1907, in Esslingen, Germany. The company was originally devoted to the production of a synthetic bating product for leather treatment. Haas was settled in the United States of America since 1901, and since the business was growing, the partners decided to open an American branch in Philadelphia in 1909, Rohm and Haas. The partnership was dissolved during WWI but was reestablished during 1920 (van Doren 1988, 1-2).

trade names according to its origin: Plexiglas® (Rohm and Haas, DE and USA), Perspex® (ICI, UK), and Lucite® (DuPont, USA). Nowadays these trademarks belong to large multinational companies that work worldwide, hence knowing the origin of an acrylic sheet by its brand is not possible anymore.

The process for producing cast acrylic sheet may have variations according to manufacturer or grade of material being produced, but generally consists in the following steps described in different publications (Altulor 1988; Cholod and Miller 1992; Stickler and Rhein 1992). The starting material may be a solution of monomer (MMA) plus initiator and other additives, or a pre-polymerized syrup containing already up to 20% of PMMA. This solution or syrup are poured into casting moulds that consist of two plane-parallel glass plates which are held apart by a flexible gasket that runs around the edge of the plates, working also as a sealing. Spring clamps hold the whole structure. The filled moulds are placed in hot-air ovens, autoclaves or hot-water tanks for polymerization. However, the conversion of MMA into PMMA cannot exceed 95 % because glasslike solidification of the reaction mixture occurs. To assure full transformation of the monomer into PMMA, it is necessary to raise the temperature above the Tg of PMMA. After cooling, the PMMA sheets are removed from the glass moulds and the surfaces are protected.

Since the artists chosen as case studies for this project have worked only with cast acrylic sheet, the production of extruded sheet will not be covered on this thesis.

1.1.2 Acrylic sheet ageing and conservation

Acrylic sheet is recognized for its outstanding resistance to weathering, being especially stable to light since pure PMMA mainly absorbs radiation under 285 nm (radiation that hardly reaches the Earth surface). Nevertheless, other chromophores, such as hydroperoxide groups, are usually present in the polymer matrix as consequence of synthesis and processing, which may absorb radiation at wavelengths higher than the polymer and initiate photodegradation reactions, as proved by the group led by Lemaire and J-L Gardette based on their longtime research on the mechanism of photooxidation of polyolefins (Lemaire et al. 1996). Photo-oxidation of PMMA has been extensively studied (e.g. Fox et al 1964; Abouelezz and Waters 1978, 1979; Gupta et al 1980; Torikai et al. 1990; Siampiringue et al. 1991; Mitsuoka et al. 1993; Rabek et al. 1995; Melo et al. 1999; Kaczmarek et al. 2000; Ferreira 2011) and is generally accepted that the polymer degrades mainly by chain scission, which is a common feature of acrylics and methacrylics with short alcoxy side groups (Melo et al. 1999; Chiantore et al. 2000; Bracci and Melo 2003). The singularity of the stability of PMMA can be further

explained by the fact that, to obtain the excellent optical properties typical of an acrylic sheet, the level of impurities must be extremely low (Davis and Sims 1983). Moreover, these impurities, or other chromophore species responsible for the initiation of photo-oxidation processes, do not have a catalytic effect. According to Sirampiguer and co-workers (Siampiringue et al 1991), the products formed in these photo-oxidation processes do not create new chromophores, which means that once the external chromophores are consumed the photo-oxidation stops (for irradiations at $\lambda > 300$ nm). These authors also suggested that in PMMA cast sheets of 3-6 mm thickness, the photooxidation would take place only in a superficial layer of ca 100 μm, because of the low permeability of oxygen in PMMA (Siampiringue et al. 1991).

Most of the photodegradation studies on PMMA have been performed on pure polymer films prepared in the laboratory, sometimes with controlled addition of other compounds/additives, and typically with radiation at $\lambda < 300$ nm to accelerate degradation. Fewer studies (Dickens et al. 1986; Siampiringue et al. 1991, Ferreira et al. 2011; Miller et al. 2013) have been conducted with industrial PMMA sheets and with radiations more similar to what an artwork may be exposed in real life. By comparing the polymer evolution under artificial ageing (Xenon light exposure, 4000 h) with natural ageing (60 months), Bracci and Melo (2003) have concluded that Xenon irruption reproduces natural ageing, contrarily to experiments carried out using irradiation with UV light with 254 nm.

Despite PMMA chemical stability, artworks in this material pose considerable challenges regarding their conservation, mainly in what concerns their surface tendency to attract dust, their high susceptibility to abrasion and scratches (Shashoua et al. 2009; de Sá et al. 2011), and the risk of having internal stress due to manufacturing and processing techniques or solvent exposure, which may lead to crazing (Sale 1993; Wright 1996; Waentig 2007; Luo et al 2007; Shashoua 2008). Therefore, most of the research related to PMMA conservation has been focused on finding effective and safe procedures for interventive conservation procedures such as adhering (Sale 1993, 1995, 2011; Roche, 2011; Laganà 2011); filling (Kim and Breitung, 2007; Laganà et al, 2017); and cleaning (Sale 1988; Murphy 2007; Casella and Moore 2009; Shashoua et al 2011; Balcar et al, 2012; Kavda et al. 2017).

1.1.3 Acrylic sheet in art

The properties of acrylic sheet such as transparency, lightweight, resistance, and ability to be moulded, that made this material suitable for aircraft canopies during World War II, were also attractive for artists, like Naum Gabo (Figure 1.2) and other

members of the Russian *avant-garde*, who felt that the recently developed plastics represented modern technological materials of the industrial era (Waentig 2002). According to Derek Pullen (1999, p. 49) "Gabo was probably the first artist to use acrylic sheet […] which he obtained in the late 1930s through his friendship with Dr John Sisson who later headed ICI Plastics." If he was "the first" or not is irrelevant but, as stated be Friederike Waentig, "in 1934 plastics-using artists such as Gabo, Antoine Pevsner and Moholy Nagy changed to Perspex and Plexiglas immediately, since they liked the better ageing properties of these materials" (Waentig 2008, p. 75). Alexander Archipenko also started to use this material in 1946 (Albus et al. 2006, p.54; Waentig 2008, p. 76) but, besides its use by these artists, PMMA and plastics in general, were practically not seen in artworks until the 1960s.

Figure 1.2: Naum Gabo, *Torsion* (1928-36), 35 x 41 x 40 cm,Tate Collection. The Work of Naum Gabo © Nina & Graham Williams / Tate, 2020. The artwork was conceived in 1928 but the actual object was constructed in London in 1936 using Perspex.

According to Albus et al., a shift in the use of plastics by artists happened during the 1960s, because "not only these materials were accessible to everyone, but also the technology for processing them, including casting, colouring, etc. Artists had a material at their disposal that had little in common with traditional working materials and was, therefore, free from all traditions and prejudices. Plastic was a modern material; it spoke of the future" (Albus et al. 2006). Therefore, during that decade, a number of artists were using plastic, mostly acrylic (Meikle 1995, p.232), which turned PMMA "almost mainstream" according to Collin Williamson (Williamson 2012). The same author refers that "PMMA was not considered as a 'plastic' and should be seen as a material in

its own right" (Williamson 2012). This profusion of artworks in acrylic may be confirmed in the Pierre Restany's book from 1973, "Le Plastique dans l'Art" (Restany 1973), in which from the 50 American and European artists covered, 20 present artworks in PMMA.

The importance of PMMA in art is noteworthy since, in the global market, this plastic is not very significant compared with others such as polyethylene, polypropylene or polyvinyl chloride (PVC) (see data available in PlasticsEurope 2020). PMMA is more expensive than any of these commodity plastics, hence its use is only justified if its special advantages can be fully exploited (Stickler and Rhein 1992, 480). This particularity may be observed when analyzing the results from the surveys conducted during the POPART project (Kenenghan et al. 2012): PMMA was the prevailing plastic in the objects surveyed from the art collections of Stadelijk Museum (Amsterdam) and Musée d'Art Modern et d'Art Contemporain, MAMAC (Nice), however, in the objects surveyed from the furniture collection of MAMAC and from the fashion collection of Musée Gallera (Paris), which were not artworks, it was almost absent.

There are no published studies regarding specifically the use of plastic in Portuguese art. In a questionnaire to Portuguese artists about the use of synthetic materials, performed by Joana Lia Ferreira, in the framework of her PhD (Ferreira 2011), 13 of the 28 artists who replied mentioned to have used acrylic glass in their work; no information is given about the dates of use of this material. According to Lúcia Matos (Matos 2016), even though during the 1960s some artists performed some experiences with plastic materials that appeared on the industry, "the means and costs of production, not to mention the limited familiarity with working techniques, prevented most artists from using these materials and the techniques associated with them". Two exceptions were Lourdes Castro (b.1930) and Ângelo de Sousa (1938-2011), two major figures of Portuguese contemporary art, from which the Department of Conservation and Restoration (DCR) of FCT NOVA has already pioneered studies on their production techniques and materials' preservation (Babo et al. 2011; Ferreira 2011; Ferreira et al. 2010, 2011, 2013). Both artists have used acrylic sheet for their artistic production during the 1960s, but they have done it in two completely different ways (Figure 1.3) and, equally important, in different contexts.

For Lourdes Castro, PMMA substituted older materials like canvas, presenting previously unattainable qualities. She was fascinated by its transparency, which would offer a perfect "immaterial" support to her shadows, as described in Chapter 2 of this thesis. She produced artworks in acrylic sheet between 1964 and 1968 while she was settled in Paris. This fact has certainly facilitated her access to this material and she used acrylic from the renowned brands Plexiglas® and Altuglas® (Ferreira 2011).

In turn, Ângelo de Sousa explored mainly the thermoplastic properties of PMMA. He was interested in the possibility of creating three-dimensional objects from a planar sheet, as illustrated in Chapter 2. Contrary to Lourdes Castro, Ângelo de Sousa was living in Portugal where, as previously mentioned, access to plastics was more difficult. The artist recalled purchasing the acrylic sheets, which were mainly sold for producing buttons, in a retail store in Porto (de Sousa 2008; Pinto de Almeida 1992; Ferreira 2011); but prior to the research developed for this thesis, nothing more was known about the origin of the material he had used.

Figure 1.3: Examples of artworks in PMMA from the two Portuguese artistes under study. On the left: Lourdes Castro, *Sombra projectada de Mílvia Maglioni* (1967), 80 x 60 cm, cut and painted PMMA (4 sheets overlaid). On the right: Ângelo de Sousa, untitled (c.1966), 29 x 47 x 25 cm, cut and curved PMMA (2 sheets).

The acrylic artworks of these two artists are the basis of this thesis. This research continues the work started in the framework of the PhD thesis of Joana Lia Ferreira (Ferreira 2011) regarding the long-term stability of Lourdes Castro's PMMA sheets. It also includes the artworks and PMMA sheets used by Ângelo de Sousa, which were studied in the framework of the protocol established between the DCR and Miguel de Sousa, the heir to the estate of the artist, to research and preserve the artist's collection, which includes the artworks, documentation left by the artist related to his production, original materials, and a library.

1.2 Scope and outline of the thesis

The main aim of this thesis is to contribute to the preservation of artworks in acrylic sheet. Because PMMA is considered a stable plastic when compared to others such as cellulose nitrate, cellulose acetate, plasticized PVC and polyurethane (Shashoua 2008), its degradation is not generally perceived as an urgent topic and it has not been the focus of many investigations, except when dealing with interventive conservation techniques as previously mentioned. The present thesis discloses a new insight into the stability of PMMA, which may be relevant for establishing new monitoring plans and preventive conservation measures, as well as to consider when testing interventive treatments in this material.

To develop effective conservation strategies for plastic artefacts, either passive or active, it is fundamental to understand the specific material composition, the techniques used in their manufacture, and the degradation processes that might be involved (van Oosten 2017). Therefore, the core of this work was to develop a thorough characterization approach for acrylic sheets used in artworks, in order to assess the impact of different formulations and industrial processes on their long-term photostabilities. To follow this goal two case studies were chosen: Lourdes Castro and Ângelo de Sousa. These artists are known for their unique work both nationally and internationally and their use of this plastic material for their artistic production in the 1960s. Because they have worked with different types of acrylic sheet and in different ways, the study of their artworks allows a broad understanding of the behaviour of this material. The research has focused on historical acrylic sheets provided by Lourdes Castro and found on Ângelo de Sousa's studio, as well as on sheets produced by two Portuguese companies, from which production processes were investigated and compared for the first time. An artificial ageing experiment was conducted in an ageing chamber under a Xenon-arc light source that simulates the solar spectrum, and a multi-analytical approach was employed for a thorough characterization, which included the assessment of visual, chemical, physical and mechanical alterations. Establishing the specific role of each additive and/or production detail in degradation mechanisms is beyond the scope of this thesis. Nevertheless, this work strived to contribute to the understanding of the importance of these aspects (encompassed in *the origin* of the material) on the stability of PMMA artworks, as well as to create awareness that this should also be considered when assessing their condition.

In the same line, the impact of surface cleaning and polishing treatments was tested in different PMMA samples. Until now, research concerning cleaning procedures for PMMA was performed in new, transparent, and uncoloured PMMA sheets, most of

the times with no assessment of long-term results. This is the first study that compares the immediate and long-term effects of the tested procedures in samples with different origins, ages, and visual effects.

From this central core of the research, two other subjects emerged which also reinforced the importance of the main goal. The first was related to the use of acrylic sheet in Portuguese art, a topic that had received far too little attention prior to this thesis. This work set out to respond to questions such as: Which artists (besides Lourdes Castro and Ângelo de Sousa) have worked with this material? How did they use it and when? What types of artworks exist? Besides, other questions arose concerning the condition of the artworks: What is the condition of the artworks (or their parts) in acrylic sheet? And what are their main problems or damages present? This thesis provides, for the first time, an overview of the use of acrylic sheet by Portuguese artists, and of the presence of this material, including its condition, in national art collections.

The other subject concerns the production of acrylic sheet in Portugal, which was triggered by the need to find out the origin of the material used by Ângelo de Sousa. The research conducted was able to uncover the history of acrylic sheet production in Portugal. In addition, it was possible to learn about the processes used to fabricate this material in the two main companies working in the country, which was fundamental to inform the research conducted regarding the stability of the different PMMA sheets.

The thesis is organized in eight Chapters that correspond to the general introduction, the presentation of the case studies, the transcription of five different published or submitted articles that reflect the holistic approach followed during this project, and the conclusion.

Chapter 1 gives a general background of the thesis and presents its scope and outline. It includes a brief introduction to the material under study that covers what is PMMA and how cast acrylic sheets are produced, its main degradation issues and the main topics researched in the conservation field so far, as well as the use of this material in art.

In **Chapter 2** the two case-studies are presented: the artists Lourdes Castro and Ângelo de Sousa. Besides providing a brief introduction to their biography and work, it is presented the information gathered related to their artworks in acrylic sheet.

Chapter 3 presents a survey on PMMA artworks conducted in the main Portuguese art collections. The results obtained provide an overview of the use of this material in art, based on 137 artworks by 69 national and international artists, represented in the 8 collections studied. The quantity and diversity of objects found

underline the importance of PMMA as an artists' material and justify research in its conservation. The results obtained have also confirmed the relevance of the two artists chosen as case-studies for this thesis. Lourdes Castro was the artist with more artworks in PMMA in the collections surveyed, and the author of the oldest artwork in this material by a Portuguese artist (1964). While Ângelo de Sousa was one of the few artists working in Portugal with PMMA during the 1960s and the author of the only artwork found during the survey with heat-formed sheets into three-dimensional shapes. The survey has also a focus on the condition assessment of the artworks and, in particular, of the PMMA elements in those artworks. In this chapter, results are presented including the main damages detected, which confirmed that PMMA is especially susceptible to dirt and dust deposits, abrasion, and scratches. This has lead to the research described in **Chapter 7**.

Chapter 4 is concerned with the origin of the PMMA used by the two artists chosen as case-studies with the final goal of assessing if differences in the sheet production will affect its properties. As previously mentioned, Lourdes Castro and Ângelo de Sousa have both worked with acrylic sheets during the 1960s, but because they were living in different contexts, the material they had access to was different. Was the material bought in Porto produced in Portugal? If so, what was the technology used? Would the material used by Lourdes Castro be of better quality than the one used by Ângelo de Sousa? In this chapter, answers to these questions are pursued. The first part describes the research conducted on the history of acrylic sheet production in Portugal and on the industrial processes used to produce it. Because there were no studies about the acrylic production in Portugal during the 1960s, research was based on primary sources of that period such as journals of the industrial field, official state publications, and in interviews with former staff members of two acrylic sheet production companies. The second part presents the characterization of artist samples (from the artists' archives) and reference samples (produced by two Portuguese companies during the 2000s), attempting to correlate differences in the material properties with differences in the production processes. Samples were characterized using several techniques: optical microscopy, infrared (FTIR-ATR) and Raman spectroscopies, size exclusion chromatography (SEC), energy dispersive X-ray fluorescence (EDXRF), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS), micro-indentation, and thermogravimetric analysis (TGA). The results obtained suggest that there is a connection between particular aspects of the production technique and the molecular and physical properties of the material.

This research is developed further in **Chapter 5**, by assessing the impact of additives and industrial production processes on the properties and long-term stability

of the PMMA sheets. The study presented in this chapter was focused on a set of samples including colourless transparent and red opaque PMMA samples provided by Lourdes Castro and similar reference samples. All samples were artificially aged in a Solar Box with irradiation $\lambda > 300$ nm for a total period of 8000 h, and alterations were followed by a multi-analytical approach, using optical microscopy, colourimetry, gravimetry, µ-FTIR, µ-Raman, SEC, micro-indentation, and TGA. In addition, samples were analyzed by thermodesorption-gas chromatography/mass spectrometry (TD-GC/MS) to identify additives and other minor compounds. The main findings are presented in this Chapter. It becomes clear that not all cast PMMA sheets present similar stabilities and that production processes (which may include the polymerization conditions, the organic additives and the origin of the monomer) play a decisive role in the properties and long-term behaviour of the acrylic sheets. Due to their particularities, the samples collected at the studio of Ângelo de Sousa were left out of this study and were characterized further in the following Chapter.

In **Chapter 6**[4], the pearlescent pigments responsible for the lustre in the PMMA sheets used by Ângelo de Sousa are identified using Raman spectroscopy. During the artificial ageing experiment conducted in the framework of this thesis, samples from these sheets have darkened in an unexpected way, showing the need for further understanding their composition and possible susceptibilities. In addition, based on the archival research performed about the artist's work, two of his sculptures appeared to have been made after the 1960s period, more precisely in c.2006 for a retrospective exhibition; the distinction of the effect pigments was a way of clarifying this issue. In this chapter, identification and characterization of plumbonacrite and bismuth oxychloride is achieved by comparison with reference materials, which needed to be synthesized for this study. The vibrational pattern (infrared and Raman) of both pigments is discussed.

Finally, in **Chapter 7,** the commercial products for cleaning and polishing PMMA sheet used by Lourdes Castro are investigated in terms of immediate and long-term effects. These ready-to-use products have possibly been developed without the same concerns conservators have. Therefore, their performance was tested and compared with the use of distilled water + non-ionic detergent, as generally recommended for cleaning plastic artefacts in museum collections. Different types of PMMA sheets were used as testing samples, the ones that have presented higher and

[4]The work presented in this chapter was developed with Eva Angelin, the main author of the correspondent article, from the samples and questions raised within the scope of the present thesis. Both authors have worked together in the different steps of data collection, synthesis of the pigment plumbonacrite, analysis of results, as well as manuscript writing.

lower photostability in the research conducted during the thesis. For the less stable testing samples, it was selected a nacreous white PMMA sheet of the 1960s, from Ângelo de Sousa's archive. Planar and curved thermoformed samples were included. This was an attempt to include "worst-case scenario" samples on testing, which could broaden the significance of the results obtained. The effect of repeated cleaning and polishing actions during the lifetime of an artwork was reproduced by submitting the samples to several cycles of cleaning and/or polishing followed by artificial ageing in a solarbox. Samples were periodically characterized by optical microscopy, colourimetry, gravimetry, μ-FTIR, μ-Raman, SEC, and micro-indentation. Results show that the impact of the treatments is not independent of the particularities of the acrylic sheet under testing. If in the "normal" samples, none of the treatments tested seemed to influence significantly their ageing; on the 1960s nacreous white samples, all treatments seemed to increase degradation during ageing. This has confirmed the importance of the research conducted during this project and presented in the previous Chapters.

Chapter 8 corresponds to the conclusion of this dissertation. It summarizes the main findings of the work and points out future perspectives for research that can contribute to the conservation of PMMA sheet artworks.

1.3 Publications within the scope of the thesis

This thesis is based on the following publications:

- S. Babo and J.L. Ferreira, **A survey on acrylic sheet in Portuguese art collections**. *Conservar Património,* (in press: https://doi.org/10.14568/cp2020075).
- S. Babo, J.L. Ferreira, A.M. Ramos, and M.J. Melo. 2017. **Back to the origins: understanding the history of production and its influence on the properties of acrylic sheet** in *Future Talks 015 – Processes. The making of design and modern art. Materials, technologies and conservation strategies*, edited by Tim Bechthold, 160-170. Die Neue Sammlung - The Design Museum. Munich. ISBN: 978-3-9818165-1-8.
- S. Babo, J.L. Ferreira, A.M. Ramos, A. Micheluz, M. Pamplona, M.H. Casimiro, L.M. Ferreira, and M.J. Melo. 2020. **Characterization and Long-Term Stability of Historical PMMA: Impact of Additives and Acrylic Sheet Industrial Production Processes**. *Polymers*, 12 (10): 2198. https://doi.org/10.3390/polym12102198.
- E.M. Angelin, S. Babo, J.L. Ferreira, and M.J. Melo. 2019. **Raman microscopy for the identification of pearlescent pigments in acrylic works of art** in *Journal of Raman Spectroscopy*, 50: 232-241. URL:https://doi.org/10.1002/jrs.5431.
- S. Babo, J.L. Ferreira, A.M. Ramos,and M.J. Melo. **Surface treatment of acrylic sheet: evaluating cleaning and polishing commercial products used by Lourdes Castro**. *Future*

Talks 019 - Surfaces. Lectures and workshops on the conservation of the Modern. Tim Bechthold, ed. Die Neue Sammlung - The Design Museum. Munich. (in press).

In addition, the following publications and conference communications have also resulted from the work developed during the thesis.

Book chapter:

- M.J. Melo, J.L. Ferreira, S. Babo, A.I. Pereira, M.E. Callapez, M.J. Àvila and J. Sarmento. 2020. **A new substance under the sun. How synthetic polymers were selected and transformed into works of art by Ângelo de Sousa, Julião Sarmento and Lourdes Castro**. In *Science and Art: The Contemporary Painted Surface*, edited by A. Sgamellotti, B.G. Brunetti, C. Miliani, 225-248. London: Royal Society of Chemistry.

Peer-reviewed articles:

- E.M. Angelin, M. Ghirardello, S. Babo, M. Picollo, L. Chelazzi, M.J. Melo, A. Nevin, G. Valentini, D. Comelli. **The multi-analytical in situ analysis of cadmium-based pigments in plastics.** *Microchemical Journal*. 157. 2020: 105004. URL: https://doi.org/10.1016/j.microc.2020.105004.

Oral communications in international conferences:

- S. Babo, J.L. Ferreira, A.M. Ramos and M.J. Melo. **Surface treatment of acrylic sheet: evaluating cleaning and polishing commercial products as used by Lourdes Castro**. *Future Talks 019 - Surfaces. Lectures and workshops on the conservation of the Modern*. Munich, 11-13 Nov 2019.
- E.M. Angelin, S. Babo, J.L. Ferreira, M.J. Melo. **Pearlescent pigments in plastic artworks: a microRaman identification**. *9th International Congress of the Application of Raman Spectroscopy in Art and Archeology*. Évora, 24-28 Oct 2017.
- S. Babo, J.L. Ferreira, A.M. Ramos, M.J. Melo. **Playing with new materials: the Portuguese acrylic sheet production and its application in artworks**. *43rd annual meeting of the International Committee for the History of Technology (ICOHTEC)*. Porto, 26-30 Jul 2016.
- S. Babo, J.L. Ferreira, A.M. Ramos, M.J. Melo. **Back to the origins: understanding the history of production and its influence on the properties of acrylic sheet.***Future Talks 015*, Munich, 28-30 Oct 2015.
- S. Babo, J.L. Ferreira, A.M. Ramos, M.J. Melo. **PMMA: Perceiving the Material in Museums and Artworks**, *Forum Kunststoffgeschichte 2014 - Plastics Heritage*. Berlin, 22-24 Oct 2014.

Panel communications in international conferences:

- S. Babo and J.L. Ferreira. **PMMA: a survey on acrylic sheet in Portuguese art collections.** *The Plastics Heritage Congress 2019*. Lisbon, 29-31 May 2019.
- S. Babo, J. L. Ferreira, A. M. Ramos, M. J. Melo. **Conservation studies on poly(methyl methacrylate): influence of industrial and artistic processes on the degradation of Portuguese artworks with acrylic sheet**.*Perspectives in Historic Polymeric Materials – Young Professionals Research Seminar (YHIP)*, Monte da Caparica, 27-28 May 2019.
- S. Babo, E.M. Angelin, J.L. Ferreira, M.J. Melo. **A taste of pearl: (re)discovering a modern lead white in PMMA sculptures**. *18th ICOM-CC Triennial Conference*. Copenhagen, 4-8 Sep 2017.

2 Case-studies

2.1 Lourdes Castro and the *Plexiglas Shadows*

2.1.1 Biography and Work

Lourdes Lourdes Castro, Figure 2.1, was born in 1930 on the island of Madeira (Portugal). As a child she studied at the German College, in Funchal, and at the age of 20 years old she left the island to study Painting at the School of Fine Arts in Lisbon, between 1950 and 1956. Due to her non-conformity with the prevailing Academicism, she did not finish the course (Curso Superior de Pintura). In the paintings she made for the evaluation of Portrait painting, she painted figures with green and blue colours instead of the common pinkish flesh tones; as result she got an "excluded" written by the professor on top of her paintings (Castro 2019).This event has triggered her will to leave the country in the hope of being able to work freely in art. Therefore, after an exhibition in Munich in 1957, she remained in Germany with the artist René Bertholo, her colleague and first husband.

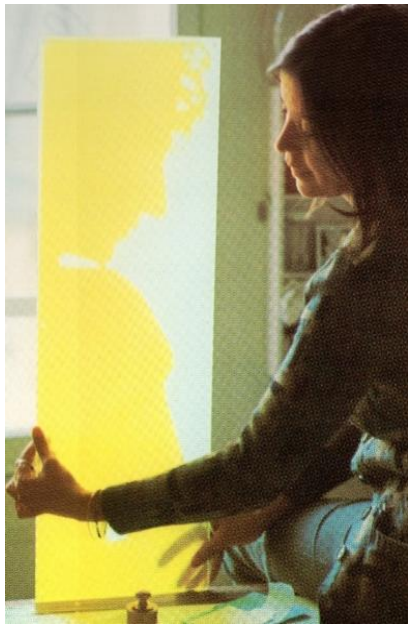


Figure 2.1: Lourdes Castro showing one of her artworks on acrylic sheet in 1967. Photo by Claude Michaelidès (Restany 1973)

In 1958 they moved and settled in Paris, with the help of a grant awarded by Fundação Calouste Gulbenkian. They were integrated in the Parisian art scene by Maria Helena Vieira da Silva and Árpád Szenes, who considered her a very promising artist (Baião 2017; Castro 2018).

In Paris, the couple founded the experimental group and magazine KWY, together with António Costa Pinheiro, Gonçalo Duarte, Jan Voss, Christo, José Escada and João Vieira (Acciaiuoli 2001). The KWY magazine, Figure 2.2, was handmade in their small apartment using serigraphy printing techniques (Candeias 2001). It relied on collaborations of friends and people they admired and, on the twelve issues that were published between 1958 and 1964, many avant-garde artists, poets and art critics were invited to contribute (Robert Filliou, Soto, Ben Patterson, Pierre Restany, Daniel Spoerri, Antonio Segui, Emmett Williams, Vieira da Silva, Helder Macedo, Herberto Helder, Nuno de Bragança, José-Augusto França, Jorge Martins, Manolo Millares, António Saura, Mário Cesariny, Pedro Tamen, Arpad, José Gil or Yves Klein, are among them). Named after the three letters that did not belong to the Portuguese alphabet, the magazine provided a platform of communication between the international artist community; it was a space of freedom and of rich artistic experimentation (Acciaiuoli 2001; Candeias 2001; Ávila 2003; Bonnin 2019).

Figure 2.2: Cover of the magazine KWY, nr.1, 1958; cover by Lourdes Castro.

After an initial incursion into the Abstractionism (Baião 2017) and probably influenced by the *Nouveau Réalism*, but more importantly by the work of Louise Nevelson (Macedo 2008), Lourdes Castro abandoned traditional painting and began to

create assemblages with everyday objects uniformly covered with paint. It was by working in these assemblages and serigraphy that the artist discovered their *shadow* and started to explore the line she has followed to the present day: the exploration of contour and shadow, Figure 2.3. As she explained: "Serigraphy is what brought my first shadows to light. I made collages with objects and I wanted to make prints, so I placed those same objects on the pre-treated silk. That is how I got actual projected shadows. I was so fascinated by the surprise of the drawing, the simplicity of the form, the outline of a shadow, its invisible presence, that I still feel it as new today. For me, a shadow has more meaning than simply the object described. It is a way of contemplating things and people around me." (Castro 2010).

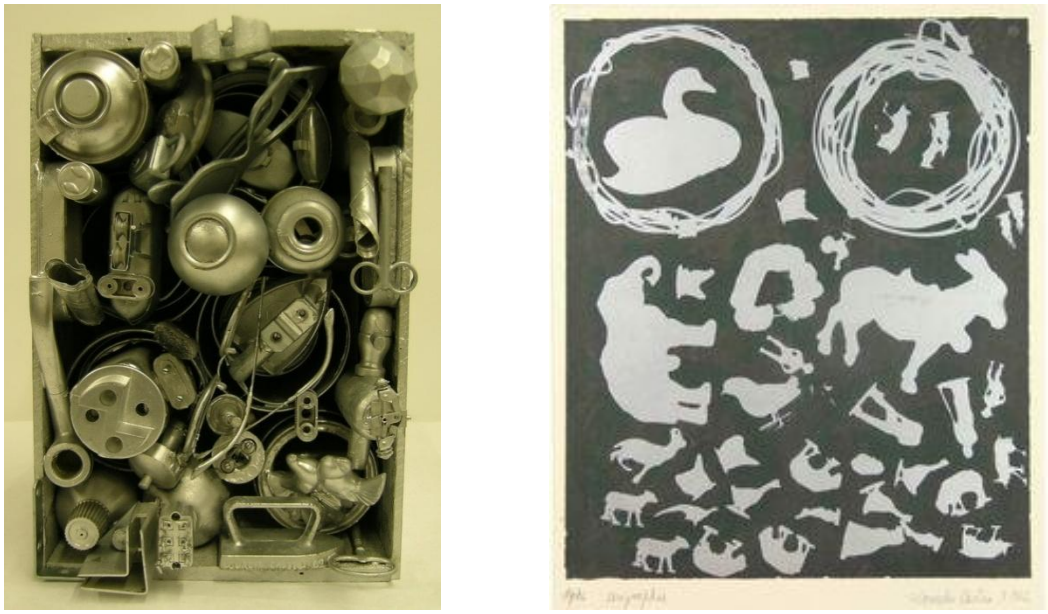


Figure 2.3: Two works by Lourdes Castro that ilustrate how the artist has started to explore the shadows in hher work. On the left, an assemblage with various materials, Caixa Aluminium (Óculos), 1962, Caixa Geral de Depósitos collection. On the right, a serigraphy on paper, Primeiras sombras projectadas, 1962, 65 x 50 cm, Artist collection.

This was the beginning of the line of work that she would continue, consistently despite the experimentation of new genres and supports, until today: "the *shadows* fascinated me in such a way that since 1962 I have been busy with shadows" (Castro 1982). In fact, from this point onwards, Lourdes Castro has been working with the shadows of friends, plants, objects and even herself (Pereira 1992). Between 1963 and 1964, the artist fixed the outline of the shadows of friends by painting it on canvas, Figure 2.4. In 1964 she started to work with acrylic sheet (Plexiglas), which she painted, cut or serigraphed, Figure 2.5. The use of this new transparent material made the

shadows "evade" from the canvas plane by being projected on the nearest wall, blending into the environment (Restany 1965).

Figure 2.4: Two works by Lourdes Castro with projected shadows painted on canvas. Left: *Sombra Projectada de Marta Minujín*, 1963, 81 x 100 cm, Centro de Arte Moderna – Fundação Calouste Gulbenkian. Right: *Sombra Projectada de Claudine Bury*, 1964, 100 x 100 cm, Museu Coleção Berardo.

Figure 2.5: Works by Lourdes Castro in acrylic sheet. Left: *In the Café*, 1964, 28 x 19 x 13 cm, Centro de Arte Moderna – Fundação Calouste Gulbenkian. Right: *Shadow of André Morain with Linhof*, 1966, 105 x 75 x 3.5 cm, private collection.

Then, between 1968 and 1970, Lourdes Castro made a series of works in which the outlines of laid people were embroidered by her in bed sheets, Figure 2.6. By doing it she questioned again some traditional artistic canons: the medium chosen is a typical feminine handcraft technique, the artworks may have a utilitarian function (they are still

bed sheets), and although they are "portraits" they may be shown in the horizontal position instead of on a vertical museum wall (Ávila 2003, 22). This tendency for dematerialization and questioning the limits of her art culminated with the theatre of shadows, a series of projects that Lourdes Castro developed between 1973 and 1985 with the artist Manuel Zimbro (Marchand 2013), her second husband. During these performances, the public observed the shadow of Lourdes Castro projected on a white screen carrying out sequences of everyday actions, Figure 2.7. There were no complicated narratives; once more, the focus was on the plasticity and on the attention to the small gestures and their transitory character. (de Freitas 1992; Marchand 2013).

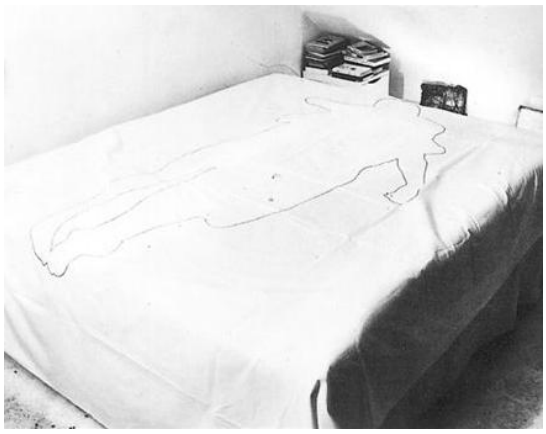


Figure 2.6: *Sombras deitadas*, 1969. Embroidered sheet, 290 x 220 cm. Museu do Chiado – Museu Nacional de Arte Contemporânea.

Figure 2.7: A view of *Linha de Horizonte* (shadows theatre), which had several presentations during 1981-1986.

About the work of Lourdes Castro, Pierre Restany (Restany 1965) and José-Augusto França (França n.d.) have highlighted the notion that by registering the outline of a shadow, the artist is fixing a passing moment, an "absence". In addition, Macedo (Macedo 2008) has stated that "the shadow is a way of investigating and working the minimum, the essential, and with elements that are part of our daily lives, which are always present but which we rarely notice".

Other significant works in her exploration of this theme are the *Grand Herbier d'Ombres* (Great Herbarium of Shadows) (1972), which consists of 100 photogenic drawings of botanic species from Madeira (Castro 2002); *Sombras à volta de um centro* (1980-1987) a series of drawings on paper of the shadows produced by flowers/plants arranged in a flower pot (Fernandes and Zimbro 2003); and *Montanha de Flores* (1988-…) an installation with geranium flowers and their petals, which have been fallen and collected by the artist since 1988 (Fernandes and Zimbro 2003). These works also reveal her profound love for nature, which dictated her permanent return to Madeira in 1983 (Coelho and Pazos-Alonso 2017).

Lourdes Castro has also produced numerous artist books since the 1950s (Pires do Vale 2015). In parallel, she has been creating her *Family Albums*, a set of books, currently numbering thirty-six, which since 1963 she has been filling with images and texts from the most diverse origins, taking as her leitmotif what has been the theme of almost all her work since then: the shadow (Culturgest 2016).

The importance of her work has been nationally and internationally recognized. She was awarded with the Medal from the Salon de Montrouge Regional Council in 1995, the EDP Lisbon Grand Prize in 2000, and the CELPA / Vieira da Silva Award in 2004. Since her first solo exhibition in 1955 in Funchal, she has showed her work numerous times in several countries. She had two major retrospective exhibitions in Portugal: *Para Além da Sombra* at the Museu Calouste Gulbenkian in Lisbon, in 1992, and *A Luz da Sombra*, which she shared with her life and work partner Manuel Zimbro, at Museu de Arte Contemporânea da Fundação de Serralves in Porto, in 2010. And more recently (2019) in France at the Musée Régional d'Art Contemporain in Sérignan, with the exhibition *Lourdes Castro, ombres et compagnie*. Her works are part of major public and private collections in Portugal and abroad, among which: Fundação Calouste Gulbenkian, Fundação Caixa Geral de Depósitos, Museu Coleção Berardo, and Museu Nacioanal de Arte Contemporânea do Chiado in Lisbon, Fundação de Serralves in Porto, Victoria and Albert Museum in London, collections of the Centre National des Arts Plastiques, Cabinet des Estampes de la BNF and Centre Georges Pompidou in Paris, Museum of Modern Art in La Havana, Museum of Modern Art Belgrade, National Museum of Warsaw and New National Museum of Monaco.

2.1.2 The Plexiglas Shadows

As previously mentioned, from 1964 until 1968 Lourdes Castro worked with PMMA sheet to create "projected shadows". Those are the works that motivated the present thesis; therefore, this next section summarizes the information gathered about them. The selected sources were published interviews with the artist (Castro 1982, 2010, 2018, 2019; Pereira 1992), exhibition catalogues and other publications dedicated to the artist (Pereira 1992; Fernandes and Zimbro 2003, da Silva 2010; Fernandes 2010; Bonnin 2018), academic thesis (Macedo 2008; Ferreira 2011; Frazão 2012), and the film *Pelas Sombras* (Mourão 2010).

About the Plexiglas, "an immaterial material"

The introduction of acrylic sheet in the artistic work of Lourdes Castro was crucial, as she explained in a text from 1966 (Pereira 1992):

Searching for a textureless material that had more to do with the result I wanted to obtain, in 1964 I created my first piece in plexiglas. At last, an immaterial material like the shadows.
It didn't make sense to continue to work on canvas. ... There was a constant dialogue between the Plexiglas and me. Because of the plexiglas' transparency and translucency, the shadows grew fainter and reprojected onto the wall. I painted underneath, cut it out, made serigraphy over it, I even engraved (books). I never wanted to mould, volume was not part of my project.
I made the shadows come out of the shadow; I gave them colours, an independent life.

For the intention of the artist, the transparency and translucency of acrylic sheet were fundamental aspects in the choice of the material. It presented advantages in relation to glass since it did not break so easily (as she explains: "It could be glass, but it breaks" (Castro 2019), it was easier to work with, and was available in numerous colours. It is important to note that the artist always uses the trade name of the company Röhm & Haas for this material, Plexiglas®. However, the term is used by her as a generic term for acrylic sheet, given that it was the first commercial name for this material in France (Leclerc 1961; Michele 2012). Lourdes Castro clarified in writing that she has also used Altuglas® acrylic sheet and, occasionally, other brands (Ferreira 2011):

Based upon availability, it was either Altuglas® (French brand) or Plexiglas® (German brand). I have never used other brands. Perspex® (English brand) rarely. In Cuba, where I made once a plexiglas, I have used a Russian brand, which was the only kind they had.

In fact, the samples loaned by the artist to DCR FCT-NOVA for the first material study conducted on her work (Ferreira 2011) were Altuglas®, and for the present study were both Plexiglas® and Altuglas®.

About the Shadows

The PMMA shadows are always of friends "who lent her their shadow" (Castro 2010). They were people with whom Lourdes Castro felt at ease. Only once did she accept a commission from someone she did not know, and afterwards she stated that she "would never do it again" (Fernandes 2010). Despite the fact that these works are personal, initially the artist has only named them as "projected shadow" or with the colour of the acrylic used. As she explained (Castro 2010):

I never used the person's name because there is a natural tendency to seek a resemblance, and that was not what I wanted. I knew that the essential characteristics were there, but I would like people to just see 'someone.' [...] However, I once wrote in a catalogue that after ten years I would identify who was who. After those ten years, I started to write the name of the people.

In these shadows, friends are usually shown performing common gestures or daily activities: reading a book, talking, smoking, combing hair, etc. Sometimes more than one person is depicted, sometimes people and objects (Figure 2.5) and sometimes only objects (Figure 2.8).

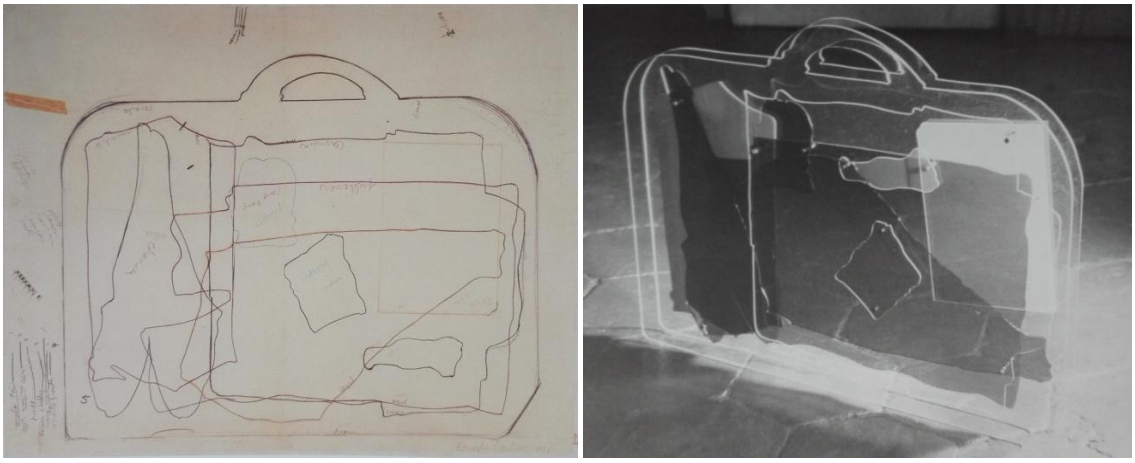


Figure 2.8: *Sombra projectada de uma mala*, 1966. On the left, the study on paper; and on the right, the artwork in cut acrylic sheet.

About the making of the Plexiglas Shadows

The process would start by drawing the projected shadow on a paper, as the artist explained (Castro 2010):

Usually, friends would come to the house for dinner and then I would put the paper on the wall and draw the shadow; from the paper I would then transfer it to canvas or later to Plexiglas. I remember one time I did an exhibition in Basel, in the same gallery as [Jean] Tinguely ... and he asked me, "How do you do this, is it from photography?" and I replied, "No, it is just drawing." He hugged me and said, "That is the way it should be done".

The drawings were then transferred to the acrylic or, more precisely, to the sticker paper that protects the acrylic sheets' surface (Castro 2019); to help in the process the artist could use carbon paper (Macedo 2008).

Figure 2.9: Sombra projectada de minha mãe, 1964.

The next step was to cut the acrylic. According to Macedo (Macedo 2008) the first work of Lourdes Castro in Plexiglas, *Projected shadow of my mother*, 1964 (Figure 2.9), was cut out with a hand saw but it was very difficult and time consuming and so, after this first experiment, the artist decided to use an electric saw to cut the acrylic sheets. Initially, she had the help of the friend Pol Bury, who had an electric saw at his house. As soon as Lourdes Castro had enough money, she bought an electric saw for her own (Castro 2019). Even so, some difficulties remained. Due to the heat produced by the saw, the PMMA would end up glued back together and had to be separated again with a manual metal saw. In an attempt to circumvent this laborious procedure, Lourdes Castro was told to drip oil from sewing machines over the drawing outlines and found that it worked, since it minimized the heat, thereby avoiding the second cut (Ferreira 2011; Castro 2019). The holes necessary to attach more than one sheet together were executed at the end. According to the information provided by the artist to Ferreira (Ferreira 2011), for finishing of the cutting edges, Lourdes Castro used iron files and then a polishing kit from *Altuglas*, first *Altupol 1* followed by *Altupol 2* (currently Altuglas Polish 1 and 2), which were applied with a cotton pad or cotton cloth. Light surface scratches were also removed with these polishing agents. As a final treatment, the artist washed the acrylic shadows with water and soap, and after drying, applied *Altunet* (currently *Altuglas Cleaner*) as an antistatic agent with a special smooth cloth. The works were signed using a pyrography tool.

The acrylic sheets could also be painted. For that, Lourdes Castro would use a glossy paint she called "glycerophthalic". The designation indicates an alkyd-based

paint, the so-called enamel paints. Sheets were painted from the back, and the artist would usually paint three layers to make it very opaque. The outlines were drawn with a fine brush and the surface painted with a wide brush or roller (Macedo 2008).

There are also numerous serigraphs and artist books in acrylic sheet by Lourdes Castro. No specific documentation was found about the process of creating the serigraphs on the plexiglas sheets, but according to information supplied by the artist, the work was performed by hand, with the help of her first partner, the artist René Bertholo.

2.2 Ângelo de Sousa and the sculptures in acrylic sheet

2.2.1 Biography and work

Ângelo de Sousa (1938–2011), Figure 2.10, was born in Lourenço Marques (now Maputo). As a teenager he developed a passion for cinema and even thought about becoming a film director, but as he could not afford the training in that area, he decided to study painting instead (de Sousa 1983, 2009). Therefore, in 1955, with the help of a grant, he moved to Porto to study painting at the Scholl of Fine Arts (Escola Superior de Belas Artes do Porto, ESBAP, now Faculdade de Belas Artes da Universidade do Porto, FBAUP). He finished the Painting course with the maximum grade, 20, and was invited to assistant professor. He conciliated his artistic career with the academic activity until his retirement as a full professor in FBAUP, in 2000.

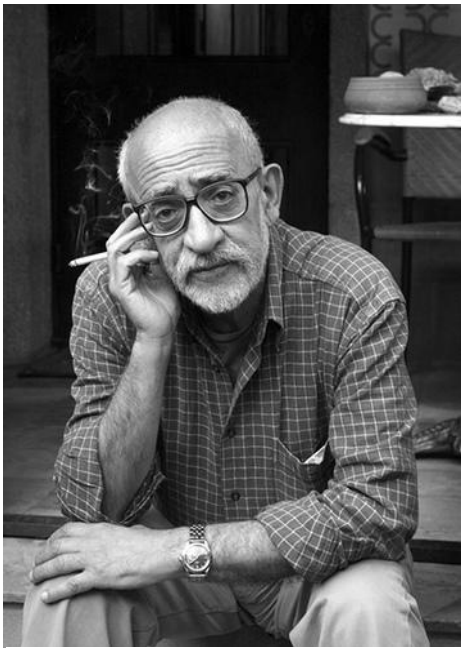


Figure 2.10: Ângelo de Sousa at his house in 2008. Photo by Egídio Santos.

Ângelo de Sousa's first exhibition was in 1959 with Almada Negreiros, at Galeria Divulgação in Porto, as part of a cycle of exhibitions in which young and renowned artists exhibited together (de Sousa 1983). He exhibited his work on a regular basis throughout his career. He was one of the founders of Cooperativa Árvore, in 1963, together with other artists and intellectuals from Porto. During the academic year 1967–1968, he attended the St. Martin School of Art and the Slade Scholl of Fine Art, in

London, with a grant from the British Council. On his return to Porto, he integrated the group "Os Quatro Vintes" (The Four Twenties) with three other colleagues from ESBAP, Armando Alves, Jorge Pinheiro and José Rodrigues, thus nominated as the four of them had graduated with the top grade. The group, without a common artistic programme, existed between 1968 and 1972, with the strategic aim of disseminating and promoting their work in an art market that was easier to penetrate with collective exhibitions (Pernes 1985).

The artistic work of Ângelo de Sousa is, by nature, abundant and diverse (Molder 2006) and he worked extensively on different artistic media including painting, drawing, sculpture, photography and film[5].Yet, it possesses a transversal nature, since the various media he explores clearly interconnect with each other (Faria 2006b), Figure 2.11–2.13. According to Bernardo Pinto de Almeida, the several manifestations of his artistic work contain an overall meaning, "the possibility of defining a body, both conceptual and visual, that could be tested in various supports" (Pinto de Almeida 1992).

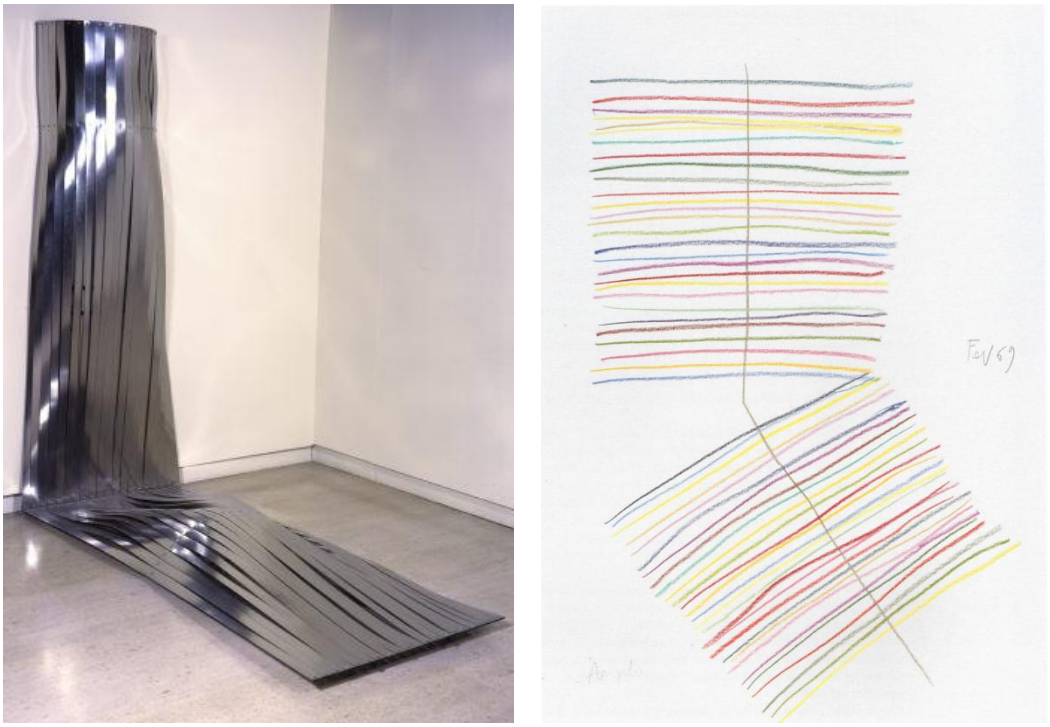


Figure 2.11: Example of artworks in different media/supports that seem to explore the same ideas. On the left, a sculpture: untitled (1968), 200x80x200 cm, iron and steel, Centro de Arte Moderna – Fundação Calouste Gulbenkian. On the right, a drawing: untitled (1969), 100x70 cm, Fundação Luso-Americana para o Desenvolvimento (FLAD) collection, pastel on paper.

[5] He even organized an happening in 1967, *To beat or not to beat*, at Teatro Experimental do Porto (Serra 2017)

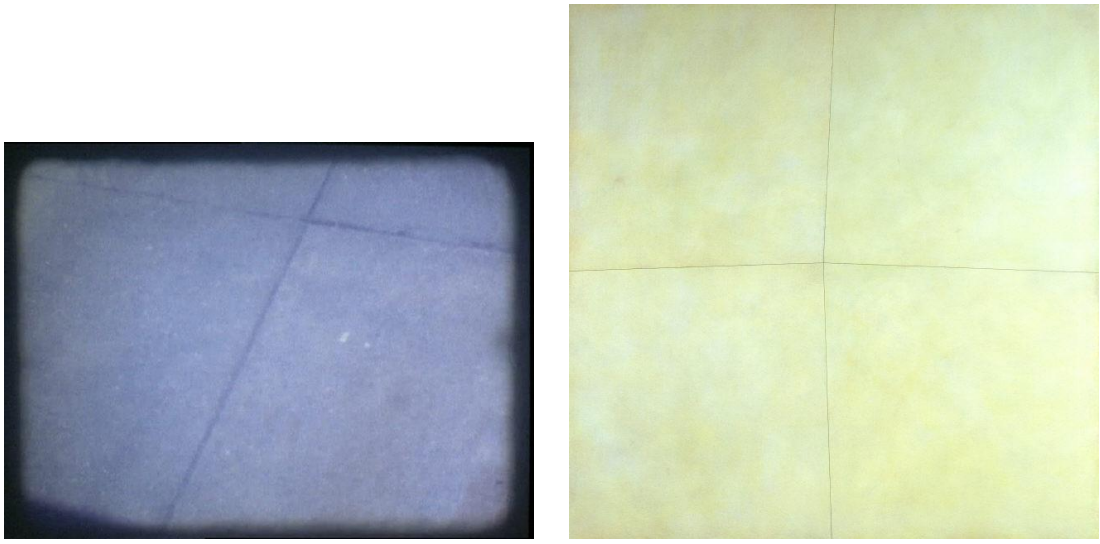


Figure 2.12: Other example of two artworks that seem to have a relation. On the left, a film: *Chão de cimento* (1972), Super8 film. On the right, a painting: 86–3–15Q (1986), 170x170 cm, acrylic on canvas. Both from Centro de Arte Moderna – Fundação Calouste Gulbenkian.

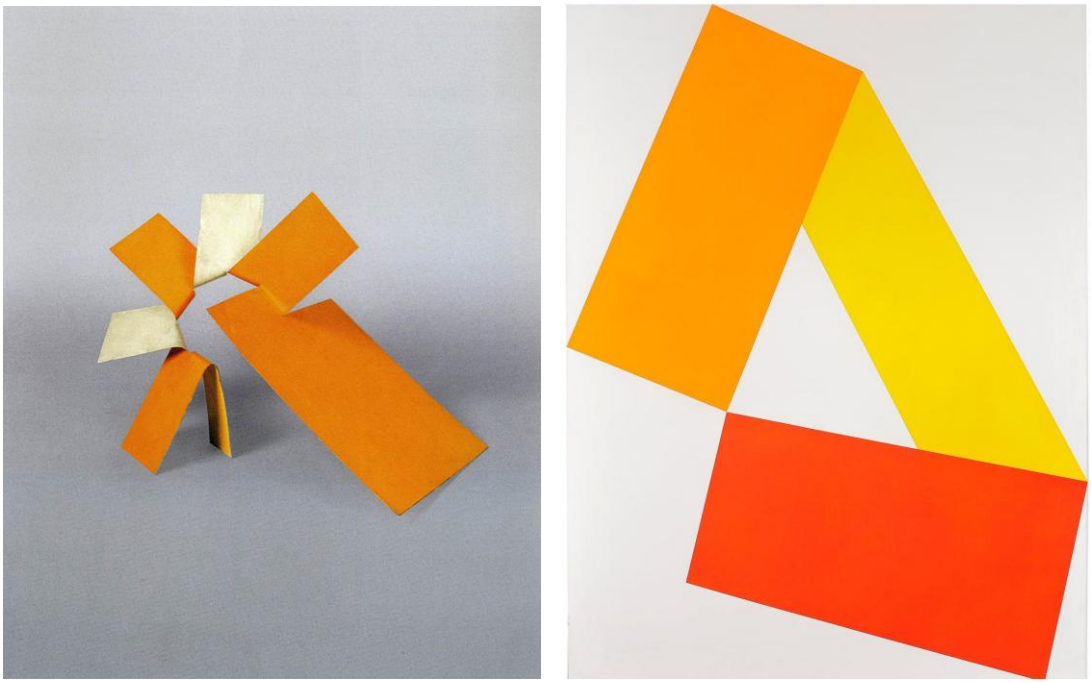


Figure 2.13: On the left, sculpture: untitled (1966–67), 35x43x26 cm, painted stainless steel, private collection. On the right, painting: untitled (2002), 150x120 cm, acrylic on canvas, private collection.

If during most part of his career, Ângelo de Sousa was mainly recognized as a painter, the importance of his work on other media has been recognized in several retrospective exhibitions during the decade of 2000: *Sem Prata*, at Museu de Arte Contemporânea de Serralves (Porto), in 2001, with film and video; *Transcrições e Orquestrações – Desenhos de Ângelo de Sousa* at Centro de Arte Moderna, Fundação

Calouste Gulbenkian (Lisbon) in 2003, with drawing; and *Ângelo de Sousa – Escultura*, at Centro de Arte Moderna and at Torreão Nascente da Cordoaria Nacional (Lisbon), in 2006, with sculpture.

The work of Ângelo de Sousa is strongly experimentalist, as recognized by several authors (e.g. Faria 2006; Pinto de Almeida 1983, 2016), however, this was not just a tendency followed by the artist, but instead it was an "absolute intrinsic necessity" (Pinto de Almeida 2015). Not surprisingly, besides exploring different media, he also explored different materials. In painting, after an initial period working with oil, casein and wax (encaustic), Ângelo de Sousa started to use a vinyl medium. Later, he used offset inks, acrylic paints and numerous drawing materials (Ferreira 2011). In sculpture, he used amongst other things, PMMA, PVC, iron, aluminium and steel.

It is important to note that this interest in exploring new materials and techniques was not only developed at an empirical level; it was also accompanied by a theoretical and technological curiosity. Therefore, he collected numerous books as well as he tried to obtain technical information directly from the industry. Ângelo de Sousa described himself as a technology enthusiast and stated that "from the time I was little, whenever I would do something, I needed to understand how it works" (Ferreira 2011). In his perspective, this search for knowledge had also practical advantages. Still in Mozambique, when he decided to become a painter, he bought a book called *How to paint in oils*, "I was not going to waste time to discover what was already discovered – it was in the book" (de Sousa 2009). Then, in his early years as a painter, not long after he arrived from Mozambique, he bought Dörner's book, *The materials of the artist and their use in painting*, which was a major investment at that time (a fifth of his monthly income). He also purchased *The Artist's Handbook of Materials and Techniques* by Ralph Mayer in 1959, and collected books about plastics. Unlike other artists, Ângelo de Sousa named precisely the materials he used, in order to supply the correct information to anyone who may need to restore his works (Ferreira 2011; Melo et al. 2020).

2.2.2 The sculptures in acrylic sheet

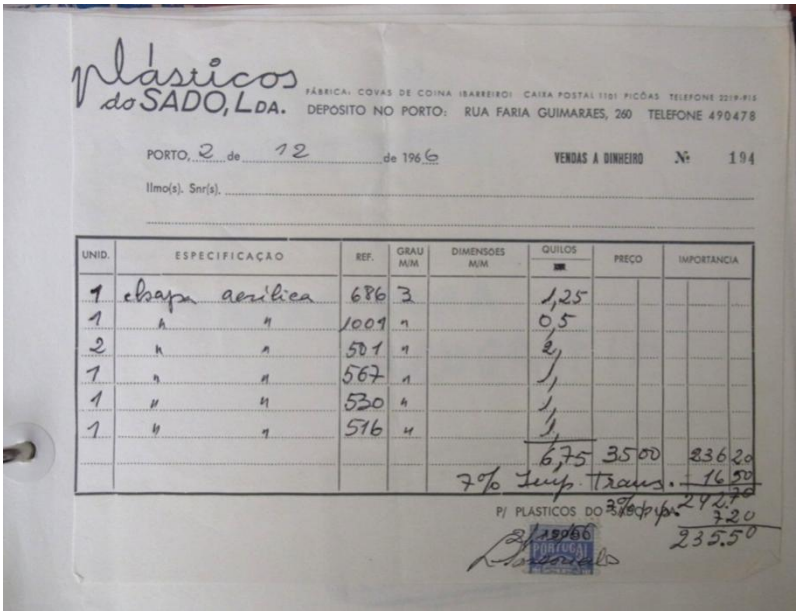
Around 1965, Ângelo de Sousa became mainly interested in Sculpture. In his particular style, he explains that this was related with the house where he lived between 1964-65 and 1972: "For some reason I could never paint [in that house]. Or because I had no light, or for anything else; and since I had to do something, I made sculpture..." (de Sousa 1992). The sculptures studied in this thesis were created during this period, using acrylic sheet. The next session presents the information collected about these sculptures, both on published texts and interviews to the author (de Sousa 1983, 1992,

2005, 2006, 2008, 2009), a report from FCG archives (de Sousa 1967), as well as from the research conducted at the artist studio.

Exploring a new material

Ângelo de Sousa recalled how he began to use acrylic sheet in one text (de Sousa 2008) and two interviews (de Sousa 1992, 2005). According to the artist, it all started around 1965, in a conversation at Café Majestic in Porto, when a gentleman said that he was selling acrylic sheets at retail in his warehouse. He and José Rodrigues (sculptor, colleague of Ângelo de Sousa) "went running to the man's shop" (de Sousa 1992, 41), and started to create a series of acrylic works "made of thin sheets, 50 x 50 cm, all in bright and blended colours […] used to manufacture buttons and decorative accessories for various purposes" (de Sousa 2008). Ângelo de Sousa mentions that he enjoyed the funny character that these vivid colours would imprint to his sculptures "I thought they were so outrages that would go very well with those apparently geometric forms" (de Sousa 2006).

An invoice found in his archive shows that the artist bought some acrylic sheets in 1966, Figure 2.14. This invoice was fundamental for the research conducted in this project because it indicates that the PMMA used by Ângelo de Sousa was produced by Plásticos do Sado, a small Portuguese company that produced acrylic sheets for the button and cutlery industries, as the artist recalled (please see Chapter 4).


Plásticos do SADO, LDA. FÁBRICA: COVAS DE COINA (BARREIRO) CAIXA POSTAL 1101 PICÕAS TELEFONE 2219-915
DEPOSITO NO PORTO: RUA FARIA GUIMARAES, 260 TELEFONE 490478

PORTO, 2 de 12 de 1966 VENDAS A DINHEIRO Nº 194

Ilmo(s). Snr(s).

UNID.	ESPECIFICAÇÃO	REF.	GRAU M/M	DIMENSÕES M/M	QUILOS	PREÇO	IMPORTÂNCIA
1	chapa acrílica	686	3		1,25		
1	"	1001	"		0,5		
2	"	501	"		2,		
1	"	567	"		1,		
1	"	530	"		1,		
1	"	516	"		1,		
					6,75	3500	236,20
					7% Imp. Trans.		16,50
							252,70
							17,20
							235,50

P/ PLÁSTICOS DO SADO

2/12/1966

PORTUGAL

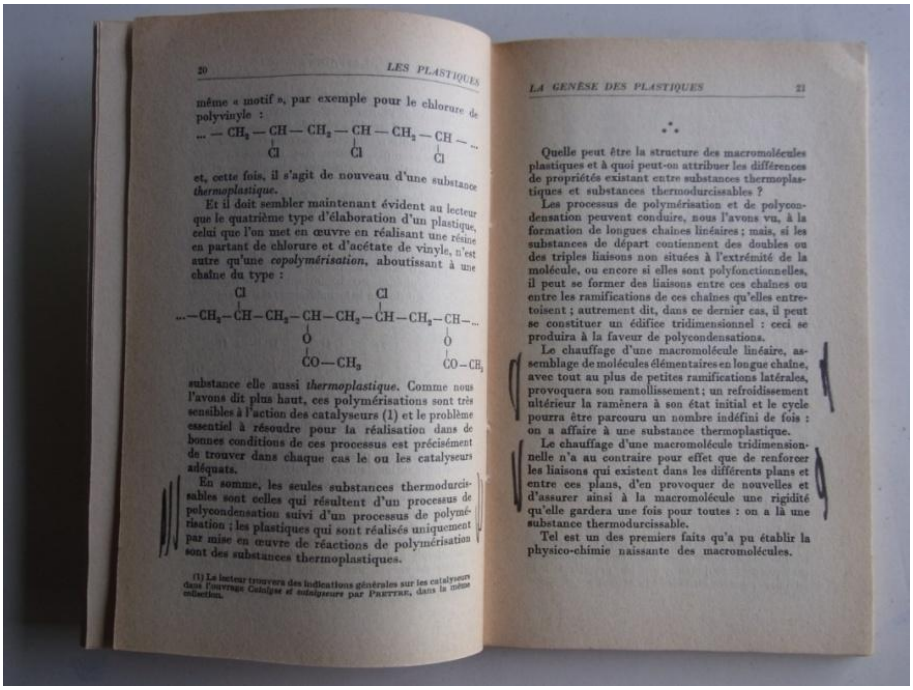
Figure 2.14: Invoice found at artist's archive, referring to several acrylic sheets bought to the company Plásticos do Sado, Porto deposit, in 2 December 1966.

This interest in exploring plastic materials for sculpture is probably an extension of what he was also doing in painting, where he was already using synthetic materials as paint binders. In a letter to FCG reporting about the studio allowance he had received during 6 months in1965, Ângelo de Sousa mentions that he had made "several trials for sculpture, in small dimensions, with plastic materials from which samples were given to me by a factory in Porto" (de Sousa 1967, 2). In the same letter he adds:

> *I would now be interested, from a more personal point of view, to continue experimenting with materials that have been created recently, such as different types of thermosetting and thermoplastic synthetic resins, respectively polyester (reinforced with glass fibre) and acrylic.*

It is interesting to note the rigor employed in the terms used to describe the materials. The explanation may be found in the library and archive of the artist, in which several international scientific and material guide books are present, as well as technical literature, Figure 2.15 and Figure 2.16. Because Ângelo de Sousa used to sign and date the books he bought as soon as he received them (Pinto de Almeida 2015), it is possible to verify that these books were acquired during the 1960s, in parallel to the practical work that he was developing. This confirms what was already mentioned about the artist regarding his researcher spirit.

Figure 2.15: The technical and scientific books found in the artist library acquired during the late 1950s and the 1960s.



20 LES PLASTIQUES

même « motif », par exemple pour le chlorure de polyvinyle :

... — CH_2 — CH — CH_2 — CH — CH_2 — CH — ...
(Cl) (Cl) (Cl)

et, cette fois, il s'agit de nouveau d'une substance *thermoplastique*.

Et il doit sembler maintenant évident au lecteur que le quatrième type d'élaboration d'un plastique, celui que l'on met en œuvre en réalisant une résine en partant de chlorure et d'acétate de vinyle, n'est autre qu'une *copolymérisation*, aboutissant à une chaîne du type :

Cl Cl
...—CH_2—CH—CH_2—CH—CH_2—CH—CH_2—CH—...
O O
CO—CH_3 CO—CH_3

substance elle aussi *thermoplastique*. Comme nous l'avons dit plus haut, ces polymérisations sont très sensibles à l'action des catalyseurs (1) et le problème essentiel à résoudre pour la réalisation dans de bonnes conditions de ces processus est précisément de trouver dans chaque cas le ou les catalyseurs adéquats.

En somme, les seules substances thermodurcissables sont celles qui résultent d'un processus de polycondensation suivi d'un processus de polymérisation ; les plastiques qui sont réalisés uniquement par mise en œuvre de réactions de polymérisation sont des substances thermoplastiques.

(1) Le lecteur trouvera des indications générales sur les catalyseurs dans l'ouvrage Catalyse et catalyseurs par PRETTRE, dans la même collection.

LA GENÈSE DES PLASTIQUES 21

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Quelle peut être la structure des macromolécules plastiques et à quoi peut-on attribuer les différences de propriétés existant entre substances thermoplastiques et substances thermodurcissables ?

Les processus de polymérisation et de polycondensation peuvent conduire, nous l'avons vu, à la formation de longues chaînes linéaires ; mais, si les substances de départ contiennent des doubles ou des triples liaisons non situées à l'extrémité de la molécule, ou encore si elles sont polyfonctionnelles, il peut se former des liaisons entre ces chaînes ou entre les ramifications de ces chaînes qu'elles entretoisent ; autrement dit, dans ce dernier cas, il peut se constituer un édifice tridimensionnel : ceci se produira à la faveur de polycondensations.

Le chauffage d'une macromolécule linéaire, assemblage de molécules élémentaires en longue chaîne, avec tout au plus de petites ramifications latérales, provoquera son ramollissement ; un refroidissement ultérieur la ramènera à son état initial et le cycle pourra être parcouru un nombre indéfini de fois : on a affaire à une substance thermoplastique.

Le chauffage d'une macromolécule tridimensionnelle n'a au contraire pour effet que de renforcer les liaisons qui existent dans les différents plans et entre ces plans, d'en provoquer de nouvelles et d'assurer ainsi à la macromolécule une rigidité qu'elle gardera une fois pour toutes : on a là une substance thermodurcissable.

Tel est un des premiers faits qu'a pu établir la physico-chimie naissante des macromolécules.

Figure 2.16: Two pages of the book *Les Plastiques* by Jean Vêne, in which some paragraphs about the differences between thermoplastics and thermosettings are marked by the artist.

The need to look for knowledge about these "new materials" in the books also stems from the difficulty in finding that knowledge by other means. In the report previously cited, the artist explains that one of the difficulties in working with plastics is "the reasonable unwillingness to provide clarification and instruction from all factories, workshops or individuals who already use these materials, accompanied, in general, by a rather limited empirical knowledge" (de Sousa 1967, 4).

Exploring a new process

The sculptures in acrylic sheet reflect the experimentalist character of the artist and also his understanding of the thermoplastic properties of the material. A brief explanation of the process for creating these sculptures was given by Ângelo de Sousa (de Sousa 2008):

> *The plates, after being heated in front of a domestic electric heater (called infrared heater) were quite soft, while warm, and they were cut and folded and bent easily. Very thick gloves were indispensable to prevent the hands from being burned.*

To better understand the process used, reproductions of one of the artworks were made at DCR during the classes of History of Art Technology and Materials, following the description by the artist, Figure 2.17. These were an opportunity to try different temperatures, cutting devices, and the time available to work with the material until it

cools down; in summary, to understand the difficulties and constrains involved in the process. It became clear that the acrylic sheets needed to be kept very close do the heater to be warm enough to be flexible, and that the process of cutting and bending needed to be very fast, otherwise the acrylic would break. It also clarified that some of the defects found on the surface of the artworks (with a bubble like appearence) are the result of overheating during the creation process.

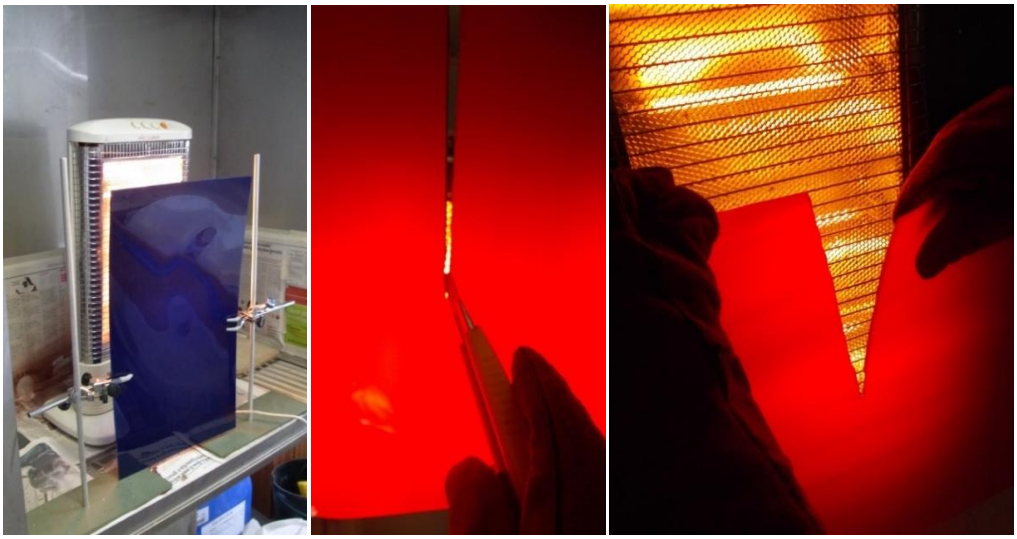


Figure 2.17: Different steps on the reproduction of the process described by Ângelo de Sousa for the making of his acrylic sculptures. From left to right: heating of the acrylic sheet in front of a domestic infrared heater, cutting and bending the sheet.

The forms obtained by the artist with this technique are very organic, some abstract and others zoomorphic (Figure 2.18 and Figure 2.19).

These sculptures were made in a small number and for a very limited period of time. Several reasons might explain this fact:

1) The cost of the material (de Sousa 1967);
2) Technical difficulties. The artist mentioned that the acrylic "would burn the hands" (de Sousa 1992) and that it "was always breaking" (de Sousa 2005);
3) Absence of an art market for them (Pinto de Almeida 2016).
4) Limited possibilities. In the type of forms that could be created, but mainly in the scale that those forms could achieve, given the small size of the sheets available and the technique that the artist was using.

About the transition to other mediums, Ângelo de Sousa wrote (de Sousa 2008):

As acrylic was expensive, I decided to do some small studies beforehand, with thin aluminium sheets [...]. Soon, I noticed that the studies were beginning to evolve into forms that would no longer be executed in acrylic and that could have bigger dimensions.

The artworks

In the research conducted, 17 artworks in PMMA were found:

- 11 artworks in moulded acrylic sheet dated from the 1960s (Figure 2.18). It was possible to confirm the date of these artworks by analyzing the photographic documentation that Ângelo de Sousa made of his work;
- 2 artworks in moulded acrylic sheet that are most probably new versions of two missing pieces from the 1960s, done by the artist in 2006, as discussed below(Figure 2.19);
- 3 moulded acrylic rods, unable to date (Figure 2.20);
- 1 artwork in flat sheets, conceived in 1985 and materialized in 2006 (Figure 2.21). This artwork was chosen from the numerous projects that Ângelo de Sousa had for artworks and created in CAM - FCG[6], for the retrospective exhibition in 2006 *Angelo de Sousa – Escultura*.

Figure 2.18: The 11 artworks in acrylic sheet dated from 1965-67, untitled. Approximated dimensions from left to right, and from top to bottom (high x width x depth, in cm): 27x55x28; 37x49x30; 29x47x25; 9x21x13; 56x27x23; 28x54x23; 22x47x26; 43x13x19,5; 24x56x28; 17,6x28x18; 27x55x55. The sculpture on the top left corner belongs to the Centro de Arte Moderna – Fundação Calouste Gulbenkian, the remaining ones to the artist's collection.

[6] During the survey done at the Modern Collection – Museu Gulbenkian (Chapter 3), remains of the sheets used to create this artwork were found. The PMMA used was Perspex®.

Figure 2.19 shows two photographs by the artist, from his archive, showing sculptures that are not found in his collection at present, and two sculptures from the collection that are most probably new versions of those ones, made by the artist for the sculpture retrospective exhibition in 2006. In an interview to Ulrich Loock (de Sousa 2006), Ângelo de Sousa refers that he had tried to remake the "dinosaur[7] with five legs" and that, "unfortunately, [the same acrylic sheets] are not for sale anymore". The dating of these two sculptures is further supported by the material research conducted in the framework of this thesis (see Chapter 6).

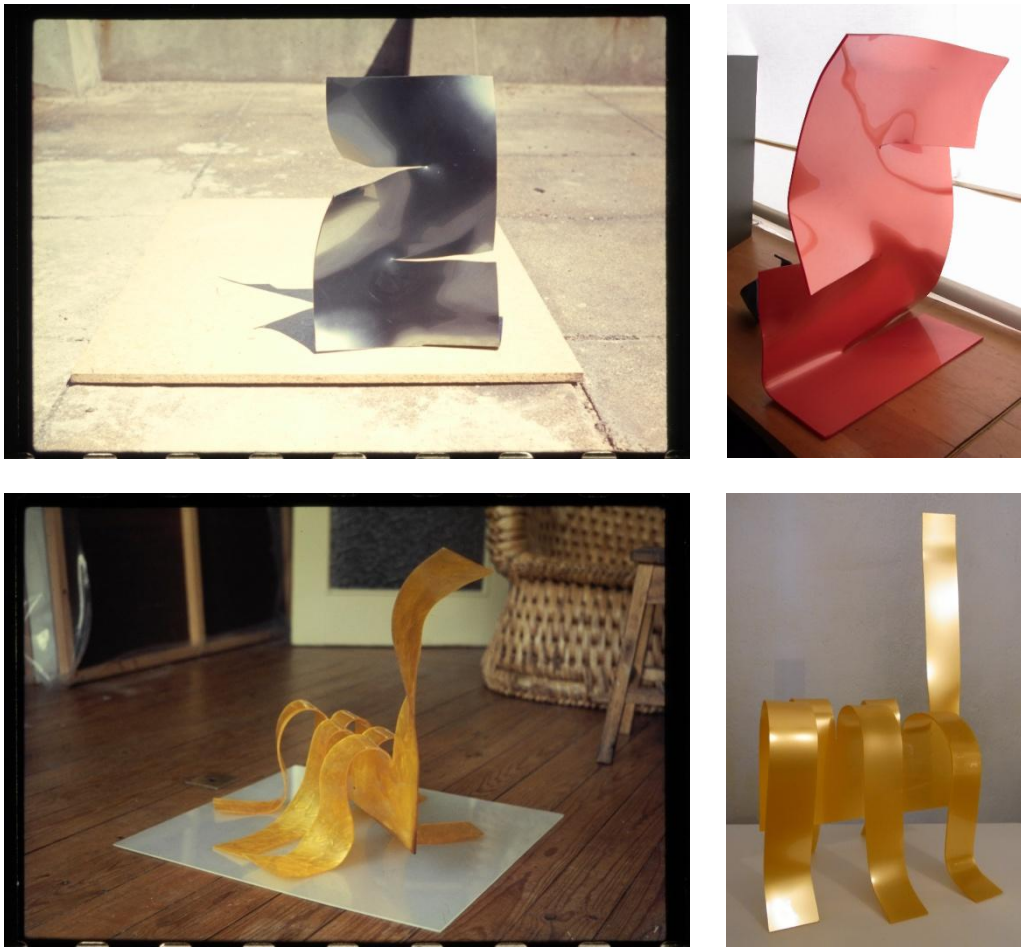


Figure 2.19: On the left, two slides from Ângelo de Sousa's archive in which two artworks not found at present appear. On the right, the new versions by the artist, most probably created in 2006.

[7] The origin of the sculpture "dinosaur" is *Gertie the Dinosaur*, a 1914 animated short film by the Winsor McCay (Wikipedia 2020). In a list with the record of his slides found in the artist's studio, Ângelo de Sousa identified the picture of this sculpture as "Gertie plástico amarelo" (Gertie yellow plastic). This reference is in line with the artist's passion for cinema and cartoons.

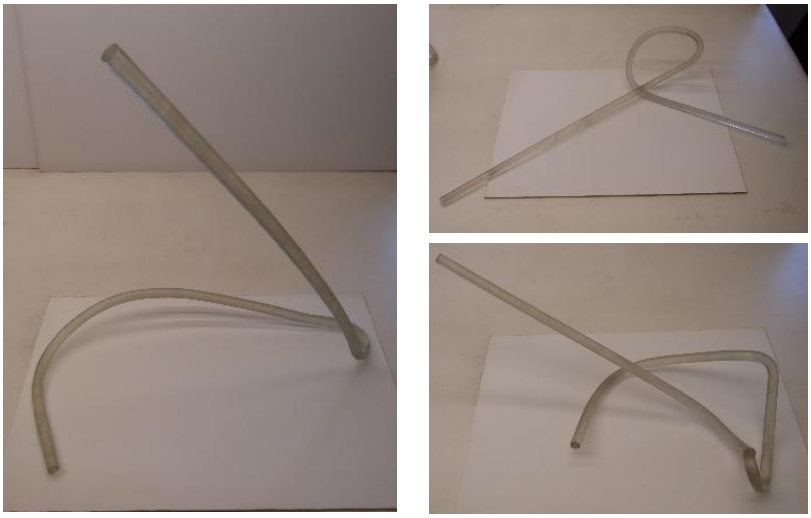


Figure 2.20: PMMA rods, not dated, maximum dimension is 40 cm, artist's collection. These rods were exhibited together in 2006 (CAM-FCG), it is not clear if they are three independent artworks or three elements of one artwork.

Figure 2.21: untitled work (1985–2006), variable size, artist's collection. Photograph by Ângelo de Sousa.

The sculptures in acrylic sheet, produced during the 1960s, despite being a small group and having been made during a short phase of Ângelo de Sousa's career, were very important for his subsequent work, for which he is more recognized. By manipulating the material as described above, the artist was researching the ways in which a flat sheet could be transformed into a three-dimensional form, a practice that he will explored further on his sculpture work with metal. Another relevant characteristic is

that these sculptures, most of the times, do not have a definite position, this is, they may be exposed in several positions, which introduces two other typical aspects of Ângelo de Sousa's sculpture: an implicit movement and a playful character (Pinto de Almeida 1983, França 1985, Gil 2006). These sculptures also reveal a profound understanding of the material and its possibilities, they reflect the capacity of Ângelo de Sousa to unveil "the imagination of matter" (to use the happy expression of Bernardo Pinto de Almeida [Pinto de Almeida 1983, 1992]), namely, by exploring the ability of PMMA to be thermoformed. This last aspect is truly innovative in the Portuguese artist context, as it is highlighted in Chapter 3.

This is an Accepted Manuscript for publication by Associação Profissional de Conservadores-Restauradores de Portugal (ARP):

S. Babo and J. L. Ferreira
'A survey of acrylic sheet in Portuguese art collections'
Conservar Património
(in press: https://doi.org/10.14568/cp2020075)

3 A survey of acrylic sheet in Portuguese art collections

Abstract

Acrylic sheet, also known by the commercial names Plexiglas or Perspex, consists of poly(methyl methacrylate) (PMMA). Attractive to artists since its development in the 1930s, it became especially popular during the 1960s. In Portugal, knowledge about its use by artists and its condition is scarce. In this work, the main Portuguese art collections were surveyed with the goal of gaining an overview of the use of acrylic sheet in the Portuguese art context and its current condition. The paper describes the methodology used and the results obtained regarding 137 artworks by 69 different artists registered as containing acrylic. Results show that this material is being used by Portuguese artists from the 1960s onwards. It has been used in several artistic forms, from painting and sculpture to photography, installation, objects/reliefs, and artist books. Most of the artworks were in good or fair condition. The main problems observed were dust and dirt deposits, abrasion, and scratches.

3.1 Introduction

Collection surveys are a fundamental tool for collection management including preservation and conservation planning. The objective and systematic data that can be generated by a survey are essential to assess and prioritize preservation needs (Patkus

2003; HCC 1998), but can also be useful in pointing out directions for research in conservation. This has been the case in the conservation of plastics artefacts, as may be confirmed by analyzing the publications in this field. During the late 1980s and early 1990s, when plastics conservation started to be seen as an urgent need and, consequently, to develop as a professional speciality, surveys were fundamental to raise awareness of the presence of these materials in several types of collections and of the problems associated to them (Then and Oakley 1993; Morgan 1994; Shashoua and Ward 1995; Keneghan 1996). Surveys have also helped to identify the most problematic plastics in collections (Morgan 1994, Keneghan 1996, 2001; Williams 2002) and to define priorities in research (Shashoua and Ward 1995; Shashoua 1999). Material identification based on date and type of object, appearance (e.g. transparency, colour, surface finish) and physical properties such as hardness and smell has been a common procedure (Morgan 1994, Keneghan 2001, Keneghan et al 2012). Nowadays, surveys in collections with plastics have become more common (Moomaw 2011; Schertel 2011; Kenenghan et al 2012; Schossler et al. 2015; Roth and Hausdorf 2019) and recent publications have been focusing on the methodologies developed for its efficient performance (Moomaw 2011; Schertel 2011; Roth and Hausdorf 2019). Unfortunately, in Portugal, this trend has not been followed and, to the best of our knowledge, there are no publications reporting the amount and condition of plastic artefacts in national collections.

One of the plastics that may be found in museum collections is acrylic sheet, which consists mainly of poly(methyl methacrylate), PMMA, and was developed industrially in the early 1930s (Brydson 1999). Due to its remarkable optical qualities, stiffness and good weathering resistance, it gained the name of "organic glass" (Aftalion 2001; Painter and Coleman 2009). Commercial names such as Plexiglas® and Perspex® are also commonly used to identify this material. In addition to its clarity and availability in different colours, other PMMA properties such as light weight and ability to be easily thermoformed, cut or glued, made this material also attractive to artists. Naum Gabo and other members of the Russian *avant-garde* were some of the few artists who started to explore the potential of this new material already in the 1930s, to substitute the less stable cellulose nitrate and cellulose acetate; but acrylic sheet was practically not seen in artworks until the 1960s, when plastics in general became widely spread in society (Waentig 2008; Albus et al. 2007).

In the conservation field, PMMA is considered a very stable plastic (Blank 1990; Melo et al. 1999; Ferreira et al. 2011; Babo et al. 2020); nevertheless, it is not immune to damage. Results from other surveys published in the literature (Lavrédine et al. 2012, 298; Lorne 1999) show that acrylic sheet objects are very susceptible to scratching.

The present work is part of a broader project which concerns the conservation of acrylic sheet in artworks. As a first step, it was considered fundamental to have an overview of the use of this material in the Portuguese art context and its current condition. Considering the lack of published information, a survey on the main Portuguese art collections was carried out. Therefore, in contrast to the most common practice, it was not intended to survey several plastics in a specific collection, but to survey a specific plastic, acrylic sheet, in several collections.

The main goals of the survey were:

- to have an overview of the artworks with acrylic sheet in Portuguese art collections (Which types of works were made? By which artists? From which dates?);
- to assess the type of acrylic sheet employed (e.g. coloured or transparent);
- to assess the condition of this material in the collections (What is its condition? What are the main damages observed?);
- to guide subsequent research to the main conservation problems observed.

This paper describes the methodology used for the survey and the results obtained. Besides providing data on artworks made with acrylic sheet, its condition and the major damages detected, it also intends to reduce the gap of knowledge about the presence of plastics in Portuguese art collections.

3.2 Methodology

3.2.1 Collections surveyed

Since the focus of this study was the use of acrylic sheet in artworks, only collections of modern and contemporary art were selected. Collections of applied arts and design were deliberately left out of this survey, even though acrylic sheet would certainly be found in these collections as well. For the survey, both public and private collections were considered as long as they are open to the general public. The main modern and contemporary art collections in Portugal were surveyed:

- Centro de Arte Moderna – Fundação Calouste Gulbenkian (CAM-FCG);
- Coleção António Cachola – Museu de Arte Contemporânea de Elvas (MACE);
- Coleção de Arte Fundação EDP (FEDP);
- Coleção da Caixa Geral de Depósitos (CGD);
- Coleção Manuel de Brito, acervo Centro de Arte Manuel de Brito (CAMB);

- Coleção de Serralves;
- Museu Coleção Berardo (MCB);
- Museu Nacional de Arte Contemporânea do Chiado (MNAC).

It is important to note that each collection has its own characteristics and specificities, which will consequently influence the results of the survey. For example, the collections of CAM-FCG, MCB and MNAC, have artworks representative of all the decades of the 20th century (Berardo Collection 2020; FCG 2021; MNAC n.d.); the collections of FEDP, CGD, CAMB, and Serralves are focused on art produced from the 1960s onwards (Fundação EDP 2017; Culturgest 2020; Gomes 2009; Serralves n.d.); and MACE collection includes mainly artworks produced in the last 25 years by artists that only started to exhibit regularly since the 1980s (Colecção António Cachola 2016). Regarding the geographic origin of the artworks or the artists represented, CAM-FCG and MCB have international collections, while the others are mainly focused in Portuguese art. CGD collection has the particularity of including contemporary art from Portuguese speaking countries, such as Brazil, Mozambique, Angola and Cape Verde (Culturges 2020).

During the survey, differences between the several collections were also found in what concerns the access to artworks, which resulted in examinations with different degrees of coverage. At MACE, MCB, CGD, CAMB, CAM-FCG and MNAC, it was possible to examine directly all the artworks registered as containing acrylic sheet, except when they were physically inaccessible. At Serralves, it was only possible to examine a selection of 10 artworks out of the 45 previously identified as containing this material; and at FEDP, it was impossible to have access and examine the artworks. Objects that were not examined directly could only be considered for the first part of this survey, and were not included in the database developed within the present survey and described hereafter.

3.2.2 Development of the survey database

A relational database was developed using FileMaker Pro 12 software, in order to input and organize all the information collected during the survey. In line with the goals previously defined, the survey was divided in two major parts: 1) Identification of artworks made of or containing parts/elements in acrylic sheet; 2) Assessing the condition of the acrylic sheet parts within those artworks and identifying its main damages. This division is reflected in the FileMaker database, which was organized in two linked parallel tables, Figure 3.1. General information from the artworks, such as author, date, typology, provenance, marks and inscriptions, materials, and general

description, was collected on the *Artworks* table. Fields for information relative to the overall condition, previous restoration treatments, storage and housing descriptions, images and other additional details were also included. The number of acrylic sheet parts/elements present in the artwork was also reported, and this field establishes a link to the files in the *Acrylic elements* table. On this second table, detailed information about each element was collected including type, colour, transparency, thickness, and transformation processes used. Data related to the condition and types of damage on the acrylic elements were gathered as well, in a total of 46 fields. When possible, the fields in the database were designed using pop-up menus, drop-down lists and checkbox sets to facilitate filling and guaranty consistency in the use of terms and grades, which helped subsequent data treatment.

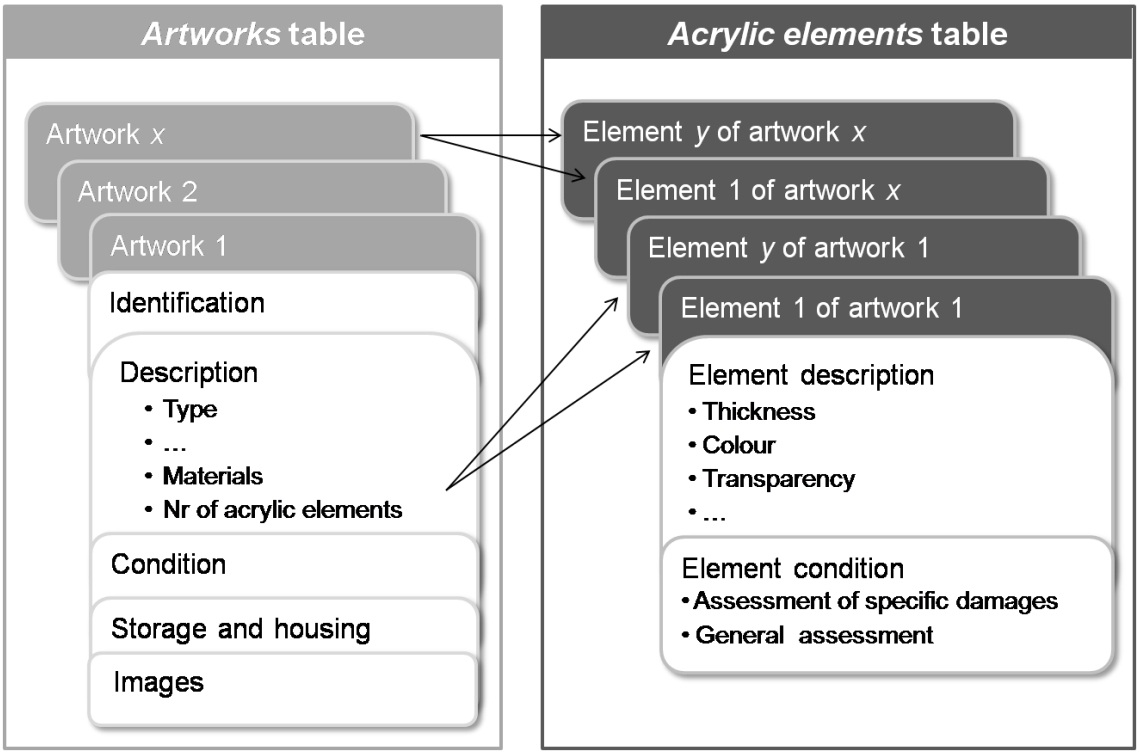


Figure 3.1: Organization of the database with the two connected tables.

Condition grades, nomenclature regarding damage types, and damage grades were based on the survey model developed in the framework of the European project POPART (Lavédrine 2012). Both artworks and acrylic elements condition were graded in one of four categories: good, fair, poor and unacceptable. Damage types were divided in three main classes: 1) colour changes, 2) deposits and 3) mechanical problems. Each specific damage (e.g. yellowing, dust, scratch) was graded in four categories:1) minor and/or limited; 2) more important but occasional; 3) general but minor; 4) severe and

general damage. More details about the grading system and description of the specific types of damage may be found in the literature (Shashoua 2008, 271-274; Kenenghan et al 2012).

3.2.3 Survey method

The survey consisted of four steps:

1) identifying all possible artworks in the collection that might contain elements in acrylic sheet;
2) examine each object and/or the respective elements in acrylic sheet;
3) adding the collected information to the database;
4) data treatment.

The first step consisted of searching for all the objects that might have acrylic sheet in each collection. This search was done previously by the conservators of the collections (in the case of CGD, CAMB, Serralves, and MNAC) or by using the collection database insitu (MCB) or online (MACE, FEDP, CM-FCG). On the collections databases, search was conducted using several terms: acrylic sheet, acrylic glass, acrylic, plexiglas, perspex, plastic, etc. It became clear that the information related to the materials of the artworks registered in the databases is often incomplete or incoherent. As a result, in some cases, artworks were added to the initial selection during the course of the second step, either by talking to the museum staff who would remember about other objects, or by finding new objects while working in the storage areas.

Any individual component of the artwork in acrylic was considered as an element. Exceptions to this rule were plinths, boxes or frame glazing that were neither original nor fundamental for the object exhibition.

Material identification was based on the museum and artist information, and eventually on examination based on appearance and feel. Acrylic sheet is a relatively simple plastic to identify since there are not many other plastics available in flat thick sheets with similar hardness and optical characteristics, as shown by the results of previous surveys. The higher price and inferior resistance to yellowing of polycarbonate does not make it an attractive alternative to PMMA for artists, while the cheaper polystyrene has inferior optical properties and is easily distinguished from PMMA by its characteristic sound when taped.

Examination of each artwork and acrylic sheet element was conducted by visual observation, with the help of raking light and optivisors. All data collected was introduced in the FileMaker database for easy consultation and exported afterwards to

Excel software. Several photographs were taken of each object, particularly of the observed damages.

This survey was conducted in different periods between 2014 and 2019.Therefore, it should be kept in mind that meanwhile more artworks with acrylic sheet may have been introduced in the collections and that the condition of some of the objects observed could have changed.

3.3 Results and discussion

During the survey, 137 artworks were identified as being made of or containing parts made of acrylic sheet. Of these, 45 belong to Serralves, 30 to CAM-FCG, 15 to CGD, 14 to MACE, 13 to FEDP, 10 to MNAC, 8 to CAMB, and 2 to MCB. Only 89 of the 137 artworks were possible to examine directly; consequently, only these were considered for the *Artworks* table in which detailed data was collected and condition assessment performed. In these 89 artworks, 244 individual elements in acrylic sheet were identified and were considered for the *Acrylic elements* table.

Images of the artworks referred may be seen on the websites of the collections, searching by the name of the authors or in Appendice 1.

3.3.1 Overview of the works of art with acrylic sheet

Several types of artworks were found which were divided by six typologies: painting, sculpture, object/relief, photography, installation, and book. This was not always straightforward since some of the artworks are in between typologies. For example, Lourdes Castro artworks were registered as paintings in CAM-FCG and as sculpture in Serralves collection. In this survey, it was decided to consider as an object/relief any artwork that should be seen on a wall (as a painting) but has an important three-dimensional component, as some of these artworks by Lourdes Castro. From the 137 artworks with acrylic sheet detected during the survey, the majority consisted of sculpture (28 %) and objects/relief (27 %). The remaining typologies are distributed in descending order as follows: painting (18 %), photography (14%), installation (12 %) and book (1 %).

Figure 3.2 presents the typologies of artworks organized per date of production. It is possible to note that the type of artworks produced in acrylic sheet has varied over the decades, reflecting the artistic tendencies of the times. For example, during the 1960s it may be seen a profusion of objects/reliefs, which resulted from the loosening of the

defined and exclusive categories of painting and sculpture that were used until then (Archer 2002) and, in particular, from the "objectualization" of painting that was followed by Portuguese artists of diverse movements during that decade (Ávila 2003, 39). Examples of artworks in this category found during the survey were produced by the British artists Peter Blake, Anthony Hill, and Gillian Wise, or by the Portuguese artists Lourdes Castro, João Vieira and Eduardo Nery.

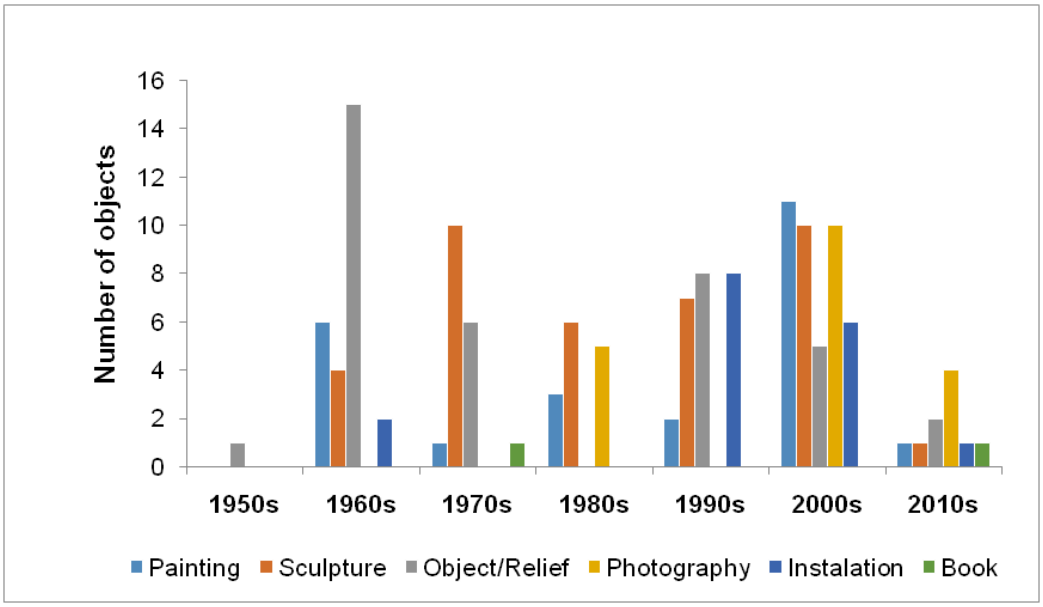


Figure 3.2: Number of artworks distributed by typology per decade of production. Total number of objects considered was 137.

The introduction of new techniques in the art field is also reflected in the results; a good example is the face-mounted photograph. This technique consists in the permanent adhesion of a sheet of PMMA to the surface of the photographic print, with either a double-sided pressure-sensitive film or a silicone rubber and primer system. The technique was developed and patented in the early 1970s, in Switzerland, as the Diasec procedure and became a tendency in photography in the mid-1980s in Germany (Penichon and Jürgens 2002). In Figure 3.2 it is possible to observe that photography typology appears during the 1980s in the collections. This results exclusively from five artworks using the Diasec process by Julia Ventura, who was working in the Netherlands during that decade. Excluding her artworks, photographs mounted with this type of technique only became common in Portugal after 2000. In fact, the Diasec process is proprietary, and very few licences were sold by the owners to other studios in the world. However, with the increased popularity of this type of mounting, similar processes that are not protected by a license were developed and started to be offered by

many more printing and mounting studios around the year 2000 (Penichon and Jürgens 2002), which may explain the results.

Regarding production dates, the majority of the artworks surveyed (31 %) was created during the first decade of the new century. Further analysis of the results displayed in Figure 3.2 shows a similar trend to what is described in the literature about the relation of plastics with art: plastic was hardly noticed as an artistic material until the 1960; it experienced a boom in the mid-1960s, when not only plastics but the technology and knowledge to process them became more accessible; its use decreased during the 1970s, partially because of health concerns but also because the feeling of novelty associated to the material was lost; and started to gain importance again after the 1980s, when it became established as just another available material in the artists' palette (Waentig 2008). The results relative to the artworks produced during the last decade (2010s) are not conclusive due to the proximity with the dates of the survey.

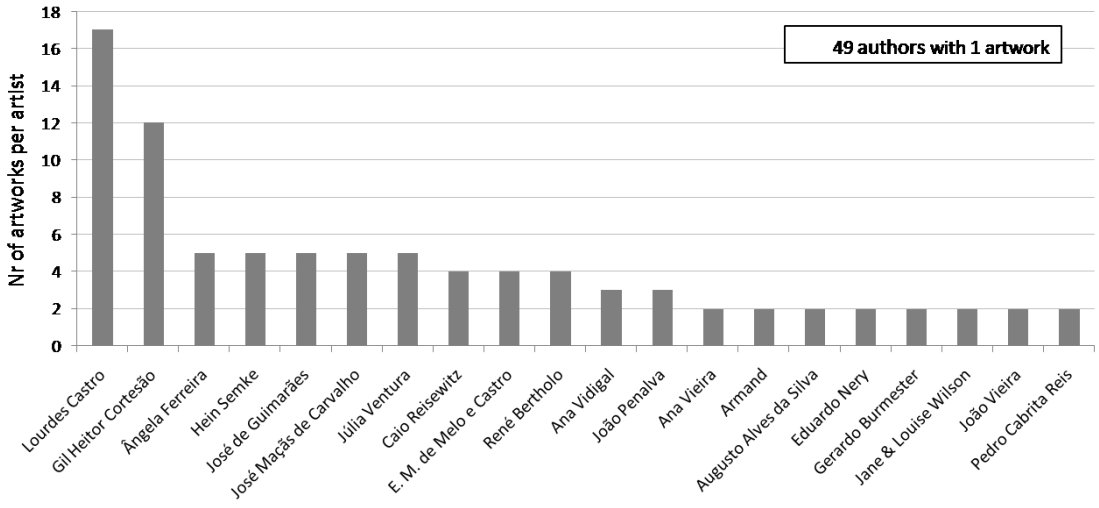


Figure 3.3: Number of artworks distributed by authors. Total number of objects considered was 137.

Besides the typology and the date of the artworks produced with acrylic sheet, it is also interesting to note which authors have chosen this material, Figure 3.3. In this survey 69 different artists were counted. Unsurprisingly, the majority was Portuguese, with 48 authors. The oldest artworks surveyed were by British artists: *White Faced Relief* (1959) by Mary Martin, *Love Wall* (1961) by Peter Blake, *Relief Construction C7(2)* (1963) by Anthony Hill, and *Relief Construction* (1964) by Gillian Wise, all from the CAM-FCG. The oldest artwork found by a Portuguese artist is from 1964, *In the Café*, by Lourdes Castro, also from CAM-FCG. The artist was working in Paris since 1958, and that has probably facilitated her access to acrylic sheet.

Interestingly, Lourdes Castro is also the most represented artist in this survey, with seventeen artworks, including fifteen paintings and objects/reliefs produced during the 1960s. Moreover, these artworks were found in all the collections surveyed except one, MACE (focused on art produced after 1980), which underlines the relevance of her work in acrylic sheet during that decade.

The second most represented artist is Gil Heitor Cortesão, with twelve paintings produced between 1998 and 2016. The artist has mastered a technique of reverse painting with oil in acrylic sheet. His paintings are present in four of the eight collections surveyed.

Reference should also be made to Ângelo de Sousa, who was a precursor in the use of this material as well. His sculpture from 1965, untitled, from CAM-FCG, has the particularity of being made with acrylic sheets modelled with heat in three-dimensional forms. This was the only artwork found during the survey using this technique.

3.3.2 Types of acrylic sheet used by the artists

Figure 3.4 presents an overview of the type of acrylic sheets used by the artists regarding transparency and colour of the material. As can be seen from the image, the majority of the elements surveyed consisted of transparent (68 %) and colourless (54 %) acrylic sheet.

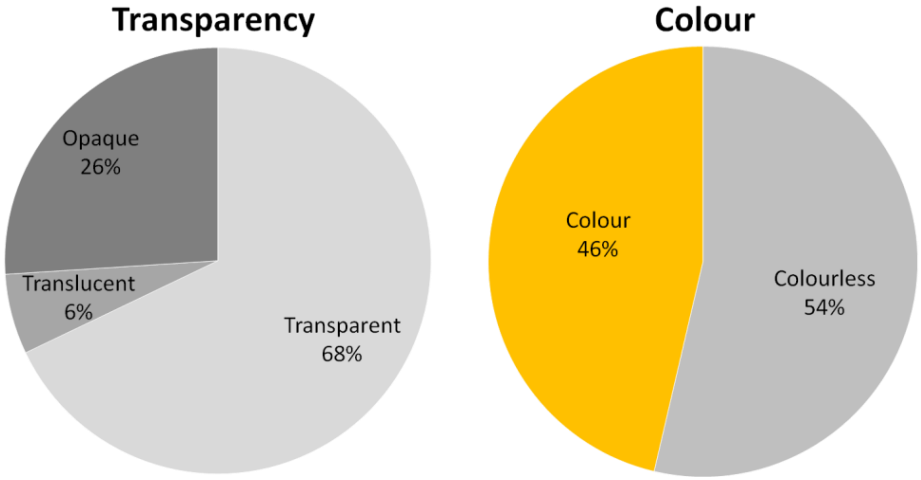


Figure 3.4: Types of acrylic sheet found during the survey regarding transparency (left) and colour (right). Total number of acrylic elements considered was 244, from 89 objects.

Acrylic sheet simultaneously transparent and colourless was the most commonly found (51%). This may be explained by the fact that, in many of the artworks observed, the acrylic was used as a painting support or as a protection barrier (as in Diasec

mounted photographs) and, therefore, "invisibility" was the characteristic preferred. In contrast, coloured elements, both opaque and transparent, were used in sculpture, object/relief and installation artworks, mostly during the 1960s and 1970s decades. Several colours were chosen by the artists, including fluorescent colours in artworks by Lourdes Castro, René Bertholo, João Vieira and Ana Hatherly (all produced between the mid-1960s and 1971), and a brilliant red in the artwork by Ângelo de Sousa (1965). The use of brilliant or lustrous sheets by Ângelo de Sousa was conditioned by the type of material available in Portugal during that period. It is known that acrylic sheets were produced mainly for the button industry and therefore there was a preponderance of lustrous sheets (Babo et al 2015; Angelin et al 2019). Regarding the thickness of the sheets surveyed, values ranging from 1 mm to 15 mm were found, but by far the majority of the sheets are of 3 mm (42.6 %).

3.3.3 Condition of the artworks and the elements in acrylic sheet

Two types of condition assessment were performed: of the artwork as a whole and of each individual acrylic element. The results obtained are summarised in Figure 3.5. Most of the artworks are in a good and fair condition (82 %), but this percentage is even higher when considering only the acrylic elements (87 %). In the other extreme are the artworks and the acrylic elements considered in an unacceptable condition, 4 % and 1 %, respectively. Acrylic elements alone are in a slightly better condition than the artworks where they belong. Artworks considered in an unacceptable condition presented severe damages such as a fracture on the acrylic sheet, but also paint delamination, which does not correspond to a bad condition of the acrylic element. Regarding the artworks evaluated in a poor condition, it should be noted that the majority corresponds to artworks produced before 1980, i.e. the group of the oldest artworks surveyed, therefore not surprising. The same tendency was observed for the acrylic elements in the same category. Artworks counted as unknown correspond to 2 installations composed of several objects, from which only the ones in acrylic sheet were observed.

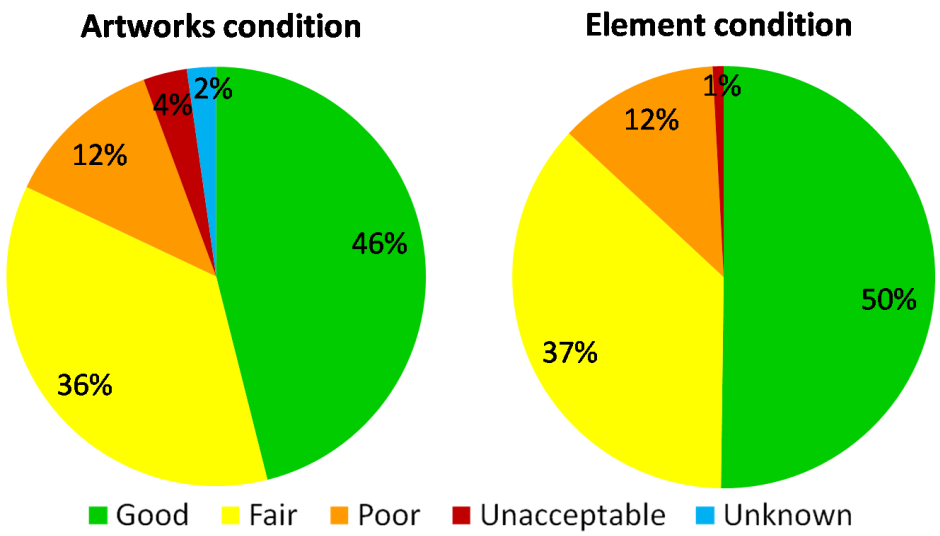


Figure 3.5: Condition of the artworks and of the elements in acrylic surveyed. Total number of artworks considered was 89 and of the elements in acrylic 244.

These values are difficult to compare with others published in the literature because data regarding specifically acrylic sheet condition are scarce and discrepant. Surveys are usually not specific to this type of plastic. As a result, in the two surveys known that present quantitative results specific for the acrylic sheet condition (art collections of the Stedelijk Museum (Kenenghan 2012) and the Pinacoteca de S. Paulo (Schossler et al 2015), the number of objects with this material was low, 18 and 15, respectively, which hinders significant results. Two other factors may contribute to the discrepancy of results. First, the condition grading of the objects is dependent on the type and period of collection (Kenenghan 2012). Second, to grade is a subjective process, and different people may evaluate the same object in different ways, even though they might be using the same scales and parameters.

Figure 3.6 provides an overview of the specific damages observed, with the number of occurrences in each grade. Damages were divided in different groups: colour changes, deposits, and mechanical problems. The most prevalent types of damage detected belong to the two last groups and were dirt and dust deposits and abrasions. Regarding dirt, finger marks were especially relevant and often observed. Abrasion was the type of damage with more "severe and general damage" (grade 4) occurrences. This agrees with what was reported in the POPART project (Lavédrine et al. 2012, 298), even though they refer to scratch only, i.e. there was no differentiation between scratch and abrasion in that study. In the same study, stain was the second most important damage observed, which was not verified in the present survey. Although breaks, or

fractures, do not present many occurrences, they are the specific damages that led to the assessment as "unacceptable condition" of 1 % of the acrylic elements surveyed (Figure 3.5), which corresponds to two acrylic sheets of two different artworks examined. Regarding colour and gloss changes, it is important to note that most of the occurrences marked in these fields were related to deposits (dust and dirt) on the acrylic surfaces, and not with a discoloration phenomenon of the material.

A relation between type of acrylic (colour, transparency, thickness) and condition or type of damages could not be established. The results show that most of the damages observed result from external factors, such as deficient housing, improper maintenance and incorrect handling.

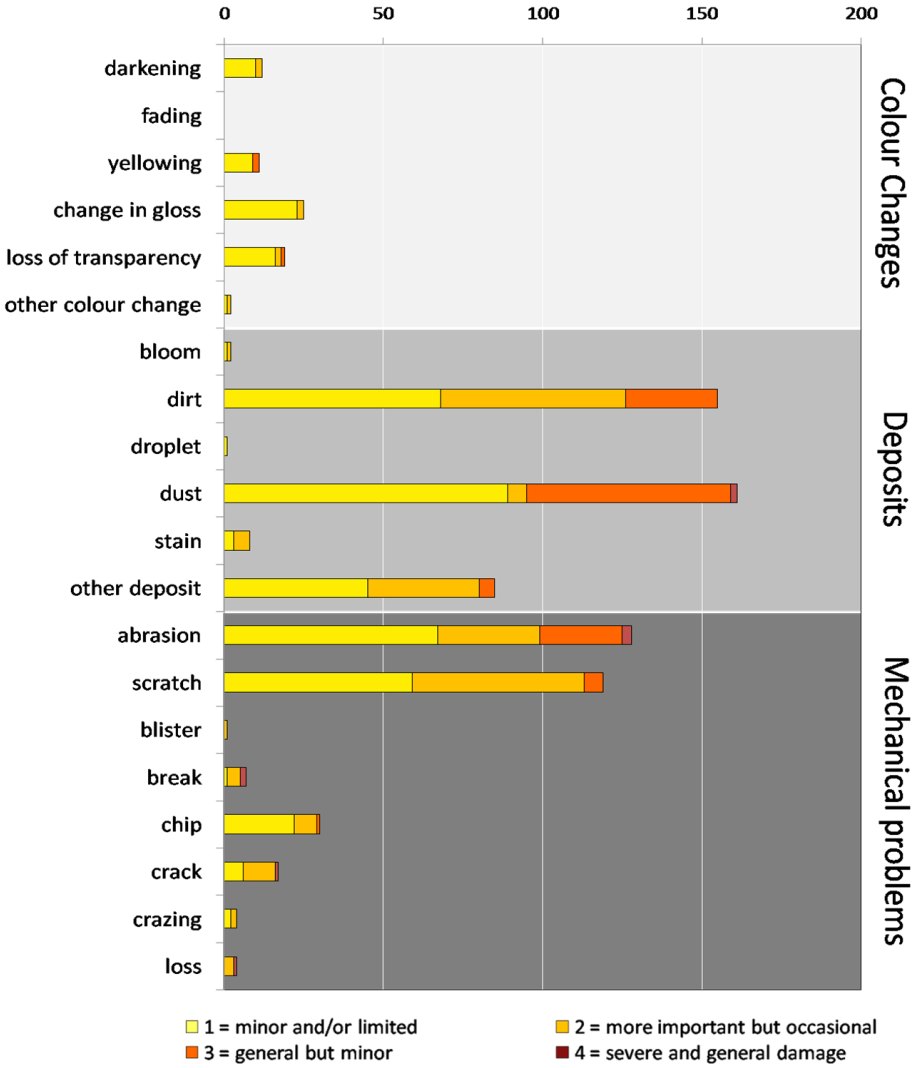


Figure 3.6: Damages observed in the acrylic elements organized in three main categories. Number of occurrences and damage grades is presented in the bars.

3.4 Conclusions

The main goals of the survey presented in this paper were to contribute to the knowledge about the use of acrylic sheet by the Portuguese artists, to assess the presence and condition of artworks made with this material in Portuguese art collections, and to identify its main damages.

The 137 artworks studied provided a general picture of the use of this material. The results have shown that acrylic sheet is a material used by the Portuguese artists from the 1960s to the present day. It was used in paintings, sculptures, objects/reliefs, photography, installations and even artist books. At least 48 Portuguese authors have used it somehow in their artworks, and from these, a more restricted group of artists has explored the properties of PMMA in a more consistent way, e.g. Lourdes Castro and Gil Heitor Cortesão. Lourdes Castro is especially relevant since she was probably the first Portuguese artist to use acrylic sheet in her artworks. Ângelo de Sousa also deserves notice for being author of the sole artwork surveyed in which acrylic sheets were transformed in three-dimensional shapes using heat.

Regarding the condition assessment, most of the artworks and acrylic elements were in good or fair condition; nonetheless some problems were detected. The main problems observed were dust and dirt deposits, abrasion and scratches, which result from a combination of known characteristics of the material (e.g. tendency to form static electricity, poor scratch resistance) and external factors such as inappropriate housing, handling and cleaning, besides eventual accidents. These results show that for the future preservation of acrylic sheet, more attention should be given to the "human factor" this is, in training museum staff in dealing with these fragile objects. In addition, given the extreme sensitivity of acrylic to abrasion and scratch, conservation research should continue on the development of safer cleaning methodologies.

As further work, it could be relevant to confirm by infrared spectroscopy if all the elements assessed are of PMMA. Although unlikely, other polymers such as polycarbonate and polystyrene could be present since they are also used to produce transparent sheets. According to other surveys (Kenenghan et al. 2012, Schossler et al. 2015), their presence in works of art is a minority in relation to PMMA.

The methodology used for this survey may be applied to other classes of plastics in similar studies. The comparison between results obtained for different plastics could be extremely interesting for several areas besides conservation and museum management, such as art history or material culture studies.

This is an Accepted Manuscript of a paper published by Die Neue Sammlung – The Design Museum:

S. Babo, J. L. Ferreira, A. M. Ramos, M. J. Melo.
‘Back to the origin: understanding the history of production and its influence on the properties of acrylic sheet’.
Future Talks 015 – Processes. The making of design and modern art. Materials technologies and conservation strategies. Ed. T. Bechthold. Munich. 2017. p.160-170
ISBN: 978-3-9818165-1-8

4 Back to the origin: understanding the history of production and its influence on the properties of acrylic sheet

Abstract

Acrylic sheet (poly(methyl methacrylate), PMMA) is a twentieth century plastic that has found worldwide applications, including artworks produced by two major Portuguese artists, Lourdes Castro (*1930) and Ângelo de Sousa (1938-2011). From 1964 until 1968, while living in Paris, Lourdes Castro worked with PMMA sheets from the well-known brands *Plexiglas*® and *Altuglas*® to produce her "shadows"; while, around the same time, Ângelo de Sousa produced sculptures with PMMA sheets purchased in Porto and likely produced by *Plásticos do Sado*, a small Portuguese company.

Would the material used by Lourdes Castro be of better quality than the one by Ângelo de Sousa? Will the production process influence the life span of the acrylic sheets? To answer these questions information on the industrial production of acrylic sheet was collected, and dated samples from both artists and different manufactures were characterised. The initial findings of this research are presented, with the joint aims of contributing to the history of plastics production in Portugal, and providing information on the material properties of PMMA from different manufacturers, in order to aid in their preservation.

4.1 Introduction

Acrylic sheet (poly(methyl methacrylate), PMMA) has been produced industrially since the mid-1930s. Depending on the manufacturer, these sheets were marketed under different trade names, such as *Plexiglas*®, *Perspex*®, *Lucite*® *or Altuglas*®. Its transparency, low weight, strength, and ability to be moulded, made it highly suitable for aircraft canopies during World War II, but also attractive to artists, such as Naum Gabo, Antoine Pevsner and László Moholy-Nagy, who were already using plastics like cellulose acetate and cellulose nitrate in their artworks, and preferred the better ageing properties of acrylic. However, PMMA only gained importance as an artist's material during the 1960s, when synthetic materials became more common in everyday life and widely accepted (Waentig 2008).

It was also during this decade that PMMA sheets began to be used by the Portuguese artists Lourdes Castro (*1930) and Ângelo de Sousa (1938-2011). Prominent figures in twentieth century Portuguese art, they were among the first to use PMMA sheets in their artistic production[8].

Lourdes Castro worked with acrylic sheets between 1964 and 1968 while living in Paris. This material was extremely important for her work because it allowed her to further explore what was already a central theme of her work – the shadow. As Lourdes Castro stated in 1966: "Searching for a material without texture and more in agreement with the result I wanted, I made in 1964 my first essay in Plexiglas. At last, an immaterial material, like the shadows. (…) I have painted underneath, cut and printed with silkscreen on the top. I even carved. I never wanted to model, since volume was not my project" (Pereira 1992).

In contrast, Ângelo de Sousa used heat to cut and model acrylic sheets in three dimensional forms (Figure 4.1). Between approximately 1965 and 1967, he explored acrylic's thermoplastic qualities; however, due to its cost and the difficulties encountered in the process of modelling with heat, he soon abandoned acrylic and turned to metal sheets.

The artworks in PMMA from both artists are particularly interesting for study. Not only because they have explored it in two completely different ways, but also because they have produced their works in different contexts (Lourdes Castro was living in Paris while Ângelo was in Porto) and therefore have used different brands of acrylic sheets. Even though Lourdes Castro always refers to her artworks as plexiglas,

[8] The main Portuguese collections of modern/contemporary art are being surveyed regarding artworks with PMMA. In the four collections surveyed so far, the oldest artworks containing PMMA by Portuguese artists were indeed by Lourdes Castro and Ângelo de Sousa.

she has stated that she has used both Plexiglas®, the German brand, and Altuglas® the French brand (Ferreira 2011)[9]. Ângelo de Sousa purchased his acrylic sheets from a retail warehouse in Porto (Pinto de Almeida 1992; Ferreira 2011), and judging from invoices found in his studio, it was most probably a store belonging to Plásticos do Sado, a small Portuguese company producing PMMA.

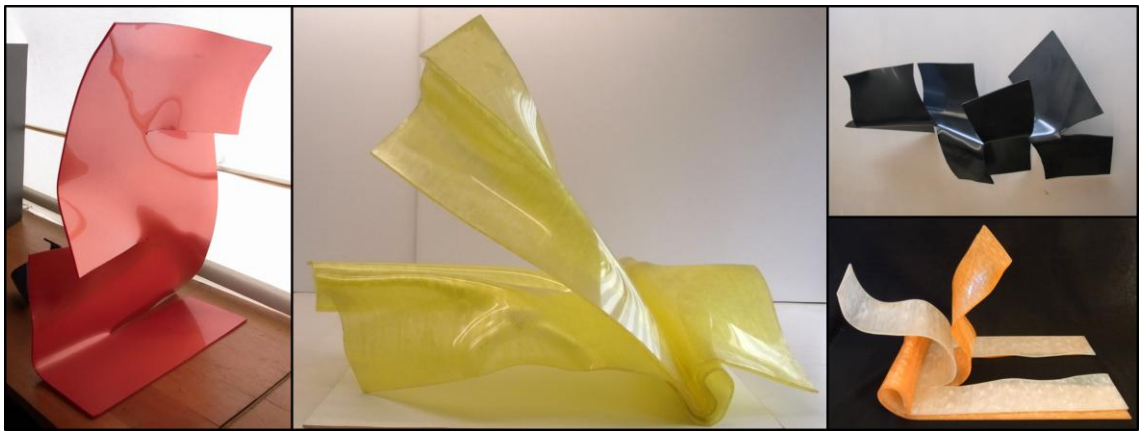


Figure 4.1: Sculptures in acrylic sheet by Ângelo de Sousa, 1965-67. Two examples in nacreous sheet are shown, at the center and bottom right.

One of the goals of this project was to understand and compare the industrial production processes used by the companies making the acrylic used by both artists. The first step was to confirm that the acrylic bought by Ângelo de Sousa in Porto had been produced by Plásticos do Sado. Initially, because so little was known about the history of plastic production and processing in Portugal, it was not even clear whether any acrylic sheet production had taken place in Portugal during the 1960s, and if so, what production technology was used? Therefore, it was necessary to study the history of acrylic sheet production in Portugal, with the final goal of assessing if differences in production affect the properties of the material and, consequently, its performance over time.

[9] In fact this distinction is not so simple. The brand Plexiglas® was created by the German company Rohm & Haas (although there was also an American branch that produced Plexiglas®) and Altuglas® was a brand of the French company Altulor. However, Altulor is the result of a merger of two companies, Ugilor and Alsthom in 1957. Until then Alsthom, through an agreement with Rohm & Haas, had produced acrylic sheet under the Plexiglas® trademark (Michel 2012). Nowadays, this distinction is even more difficult since both trademarks belong to large multinational companies: Evonik owns the production and commercial rights of Plexiglas® everywhere except on the American continent (where rights belong to Arkema); Arkema in turn owns Altuglas® rights for the rest of the world.

4.2 Methodology

Research on the history of PMMA sheet production in Portugal (from 1950s onwards) was conducted in parallel with material characterisation of the PMMA samples. The historical research involved interviews with two individuals who worked in acrylic sheet production in Portugal: Sónia Apkan (daughter of Plásticos do Sado founder and owner until its closing in 2009) and Carlos Carvalheira (a chemist who worked at Paraglas between 1990 and 2008). Their information was complemented with documentary sources. The primary sources consulted were: *Plásticos*, the journal of the Portuguese plastics industry, covering the period between 1967-1978; *Boletim da Direcção-Geral dos Serviços Industriais* (DGSI bulletins), an official journal of industry regulations published weekly by the Portuguese Ministry of Economy (volumes between 1955-1965 were consulted); and copies of the official registration of the companies in the Commercial Registry Office – Ministry of Justice.

DGSI bulletins were an important source of information. In the period between 1931 and 1974, the authoritarian regime of *Estado Novo* implemented an industrial protectionist policy in Portugal (Regime do Condicionamento Industrial). Therefore, introduction of new industrial plants, installation of new equipment, or any changes in technology were subjected to authorisation by the state. All requests, possible opposition from other industrials, and dispatches from the government were published in the DGSI weekly bulletins.

Regarding the material characterisation, the main goal was to compare relevant properties that could be associated with each production process. Therefore, dated samples from Plásticos do Sado and Paraglas (companies from which the production processes employed were known in more detail due to the historical research) were selected as well as samples from the 1960s from both artists. Lourdes Castro provided transparent and opaque red samples, hand-marked as Plexiglas® and Altuglas® respectively. From the Portuguese manufacturers similar samples were selected. From Ângelo de Sousa nacreous (pearlescent) sheets corresponding to the ones used in his artworks were found in his studio. This way, three groups of samples were studied - transparent, opaque red, and nacreous (Table 4.1).

Samples were characterised using several techniques: optical microscopy, infrared spectroscopy (FTIR-ATR), Raman microspectroscopy (μ-Raman), size exclusion chromatography (SEC), energy dispersive X-ray fluorescence (EDXRF), scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS), microindentation, and thermogravimetric analysis (TGA) (please see Chapter 5 for details).

Table 4.1: Identification of the samples studied[10].

Brand	Colour/opacity/ref	Origin	Date	Identification	Group
Plexiglas[a]	Colourless/transparent	Lourdes Castro	1960s	LC/Plexiglas	
Plásticos do Sado	Colourless/transparent	DCR	2000s	P.Sado_trp	Transparent
Paraglas	Colourless/transparent		2000s	Paraglas_trp	
Altuglas[a]	Red/opaque	LourdesCastro	1960s	LC/Altuglas	
Plásticos do Sado	Red/opaque/9081	DCR	1990s	P.Sado_9081	Red
	Red/opaque/9082		1990s	P.Sado_9082	
Paraglas	Red/opaque/6470		2000s	Paraglas_6470	
	Red/opaque/6500		2000s	Paraglas_6500	
	Red/opaque/6700		2000s	Paraglas_6700	
Plásticos do Sado[b]	White/nacreous	Ângelo de Sousa	1960s	AS/P.Sado_w.nac	Nacreous
	Yellow/nacreous		1960s	AS/P.Sado_y.nac	
	Orange/nacreous		1960s	AS/P.Sado_o.nac	

[a] According to the artist.

[b] According to characteristics of the sheet and an invoice found.

4.3 Production of PMMA in Portugal

4.3.1 Historical overview

Based on the analysis of information published in DGSI bulletins from 1955 until 1965 regarding authorisation for the production of plastic materials and respective opposition, it was possible to conclude that at least four companies existed in Portugal producing PMMA during the 1960s.

The oldest was Luso-Sintética Lda. (located in Portela de Sacavém, in the outskirts of Lisbon), which was registered at the Commercial Registry Office of Lisbon in 1955 when it started business. Its business license in 1957 described it as a "factory of acrylic plastic material (methyl methacrylate) namely boards, sheets and bars" (DGSI 1958). According to a study from 1960 about the plastic industry (Guimarães 1960), aside from semi-finished acrylic products, Luso-Sintética also produced the acrylic monomer through the depolymerisation of acrylic residues, which were used for their

[10] In the next chapters of this thesis, shorter identification codes were used for selected samples. Correspondence as follows: LC/Plexiglas = TPL; P.Sado_trp = TPS; Paraglas_trp = TPA; LC/Plexiglas = RAL; P.Sado_9081 = RPS; Paraglas_6500 = RPA; AS/P.Sado_w.nac = NW.

own production of nacreous acrylic sheets. This information is further confirmed by a dispatch from 1964 (DGSI 1964a*)* where the firm is authorized for "the installation of a distillation retort, of 200kg of capacity." Distillation is a fundamental step to obtain pure MMA through chemical recycling.

The second oldest company appears to be Plásticos do Sado. The registration at the Commercial Registry Office of Lisbon is December 1961, but there is a reference that the business started in September 1959. In fact, a reference appears in a DGSI bulletin from 1959 that probably relates to Plásticos do Sado, as it mentions the name of one of their partners. This reference concerns a request for permission to install "a setup for distillation of residues of methyl methacrylate" in their "factory of plastic articles" (DGSI 1959), which was authorised by DGSI in the following year (DGSI 1960a). In a request for transferring the factory from Setúbal (its original location) to Lisbon dated from 1962 (DGSI 1962b), the business is already described as "a factory of plastics, acrylics, distillation of methyl methacrylate residues and workshop".

Recycling PMMA residues to produce monomer for further polymerisation into PMMA sheets appears to be typical for that period in Portugal. In a request dated from the end of 1962 (DGSI 1962c) a third company, named Ipacril-Indústria de Produtos Acrílicos, Lda., askes for authorisation to set up "an installation for recovery of polymethyl metacrylate waste (acrylic sheet waste) into methyl methacrylate monomer", which was authorised in 1964 (DGSI 1964a). According to its registration at the Commercial Registry Office of Loures, Ipacril was in operation since August 1961. The fourth and last company operating during the 1960s was Socril, although no registration was identified by that name in the Commercial Registry Offices. Company representatives presented a request for installing a factory of acrylic glass in the north of Portugal in 1960 (DGSI 1960b), which was authorised under the condition that Socril would not produce monomers or nacreous sheets (DGSI 1960c). However, from the following sequence of transference requests (DGSI 1961, 1962a, 1964b), it appears that the factory was only installed after 1964, and at a different place in Santarém district. Further research in the *Plásticos* journal (in the published list of plastic manufactures enrolled in the guild) made it possible to conclude that in 1969 this factory became Paraglas[11]. This helps to explain the statement by Carlos Carvalheira (2015) during his interview, that Paraglas started around 1962-65 and that it was sold to the German company Degussa in 1969. In fact, the original name of the company operating in 1964 was Socril, becoming Paraglas in 1969 (according to the registration at Commercial

[11] In the list of plastic manufacturers published in *Plásticos,* nr 11, Jan-Mar 1970, Socril disappears and Paraglas appears for the first time. The address of both companies is the same.

Registry Office of Benavente, Paraglas started to operate in November 1969 and Degussa is referred to as one of the shareholders).

From these four companies only two have survived: Plásticos do Sado and Paraglas[12]. They merged in 2005 and stopped production in 2009. With this closure the production of PMMA in Portugal ended.

4.3.2 Plásticos do Sado

According to Sónia Apkan (2015), Plásticos do Sado was founded by an Armenian entrepreneur, Jirayer Apkan, who, after travelling to different countries, decided to settle and start a business in Portugal, probably during the 1950s. Most likely he had visited a PMMA manufacturing plant in Germany but he did not have any specific education or training in this area. His business started with the production of acrylic sheet for the button industry and, for this reason, nacreous sheets were particularly relevant. It was always a family business, with small-scale production using a basic technology. The production process used at Plásticos do Sado was similar to what is generally described for the production of cast PMMA sheet (cf. Stickler and Rhein 1992). It consisted of introducing a pre-polymerised syrup of MMA into glass moulds (formed by two parallel polished glass plates which are held apart by a flexible gasket of PVC and metal clamps); heating the moulds with the syrup for polymerisation in water tanks; and then removing the solid sheets from the moulds (Apkan 2015).

As noted above, the monomer used was also produced in the factory through chemical recycling (depolymerisation) of PMMA. For that, scrap plastic from their own stock as well as from other retailers was used, including scrap purchased abroad, mainly from the production of automotive lighting. Depolymerisation was carried out by pyrolysis in a reactor with a molten lead bath (Carvalheira 2015), where the PMMA was heated to about 400^{o}C (Rosa and Barros 1999). The resulting MMA was collected in a condensation system, after which several steps of washing, decantation, and distillation were necessary to obtain a pure enough monomer to produce acrylic sheets. Most of these steps were controlled visually, based on empirical knowledge (Apkan 2015; Rosa and Barros 1999). For transparent sheets, special care had to be taken with the purity of the MMA, but "good enough" monomer could be used to produce opaque dark sheets (Apkan 2015).

[12] A bankruptcy note from 1981 appears in the Ipacril registration process, indicating the end of the company. Regarding Luso-sintética, although no changes were made to its registration process, we may assume that this company has also closed since no signs of its recent existence were found.

The following information comes mainly from an internship report made in 1999 (Rosa and Barros 1999), however, according to Sónia Apkan, the original processes remained unchanged, so the information may reflect what was done in the 1960s. The prepolymerised syrup was prepared by adding in a reactor the distilled MMA, an initiator (azobisisobutyronitrile, AIBN), a release agent (stearic acid) and a plasticiser (bis(2ethylhexyl) phthalate), and heating the reactor up to 88°C while stirring. The duration of this reaction and the viscosity of the reaction mixture was empirically controlled, which meant that the resin obtained did not always have the same molecular weight and therefore the same viscosity. Colourants and anti-UV agents could then be added to the syrup, which was then poured into the glass moulds, already in the water tanks. The polymerisation occurred in water at around 60°C and would take 8-12 hours (Rosa and Barros 1999). After this first step the temperature was raised while the polymerisation continued in the water tank. After cooling, PMMA sheets were removed from the moulds and both surfaces protected, initially with a paper adhered with glue applied by brush and later on by a polyethylene film applied mechanically (Apkan 2015).

4.3.3 Production processes overview

Technical information about the production of PMMA sheet at Paraglas was also collected during the interview with Carlos Carvalheira (2015). Even though PMMA from this company was probably not used in the artworks of Lourdes Castro and Ângelo de Sousa, the study of its production process is interesting, as it was one of the few companies to have produced this material in Portugal until recently. Likely because of its relationship to Degussa, the process used is more technological and controlled, closer to the descriptions in the literature than the one from Plásticos do Sado. Because of these reasons a comparison between both is especially interesting.

Access to primary sources with detailed descriptions of the processes used to produce Plexiglas® and Altuglas® was not possible, however, a work by Jean-Marie Michel (2012) provides a considerable amount of information about PMMA production in France and it was used as a possible indication of the French Altulor process.

Table 4.2 summarises some of the particularities of each step in the production of cast PMMA sheets by Plásticos do Sado, Paraglas and Altulor. Some differences between the processes are evident:

- the use of recycled monomer and the lack of control of the degree of polymerisation in the pre-polymerised MMA syrup used by Plásticos do Sado;

- the use of the Rostero process5 by Paraglas, which allowed greater control of the temperature and consequently of the reaction.
- the fact that at Plásticos do Sado the second step of polymerisation was below
- 100°C. It is known that in the first step of polymerisation conversion only reaches 80-90% because glasslike solidification of the reaction mixture occurs preventing higher conversion values. To assure full transformation of the monomer into PMMA, it is necessary to raise the temperature above the Tg of PMMA, to 110°C-120°C (Stickler and Rhein 1992).

Table 4.2: Main characteristics of the production of PMMA sheets in three different plants

	Plásticos do Sado (Apkan 2015, Rosa and Barros 1999)	**Paraglas (Carvalheira 2015)**	**Altulor (Altuglas) (Michel 2012)**
Monomer	Produced by the company through chemical recycling	Pure monomer acquired from Degussa or Repsol	Produced by the company (synthesis by the Ugilor process)
Solution poured into the moulds	Pre-polymerized syrup (degree of polymerisation empirically tested, prepared by heating the monomer at 88°C with initiator AIBN)	Monomer solution (MMA + initiator AIBN)	Pre-polymerized syrup (8-10% of PMMA, prepared by heating the monomer at 80/90°C with initiator AIBN)
Polymerisation	Polymerisation in water tanks. Moulds are placed vertically in hot water tanks and heated at 50-60°C	Rostero process. Moulds are held vertically between metallic plates, which allow accurate control of temperature; placed in a chamber with pressure control and heated to 75-80 °C.	Polymerisation in heated chambers or water tanks. Moulds are placed horizontally in containers and heated at 50-60 °C.
	Polymerisation is completed at higher temperature, but still in the water tank (<100°C)	The polymerisation is completed by heating at 120°C (postpolymerisation)	The polymerisation is completed by heating at 120°C (postpolymerisation)

4.4 Material characterisation: molecular and physical properties

Polymer matrixes of all samples were characterised by infrared spectroscopy as PMMA homopolymer, which confirmed that all samples were in fact acrylic sheet. Cross-sections of all coloured samples were prepared and examined by optical microscopy using different light spectra (visible and UV) and conditions. This allowed

insight into the pigment distribution in the polymer matrix and also to screen for the presence of organic dyes as they fluoresce under UV light. Only individual particles or small agglomerates were observed (Figure 4.2) and, although their colour is widely diffused in the polymer matrix, they are present in very small quantities, which hinders their identification. Further analysis of selected samples by SEM-EDS provided images where the distribution and low amount of inorganic material present became more evident (Figure 4.2), likely present in amounts lower than 1%.

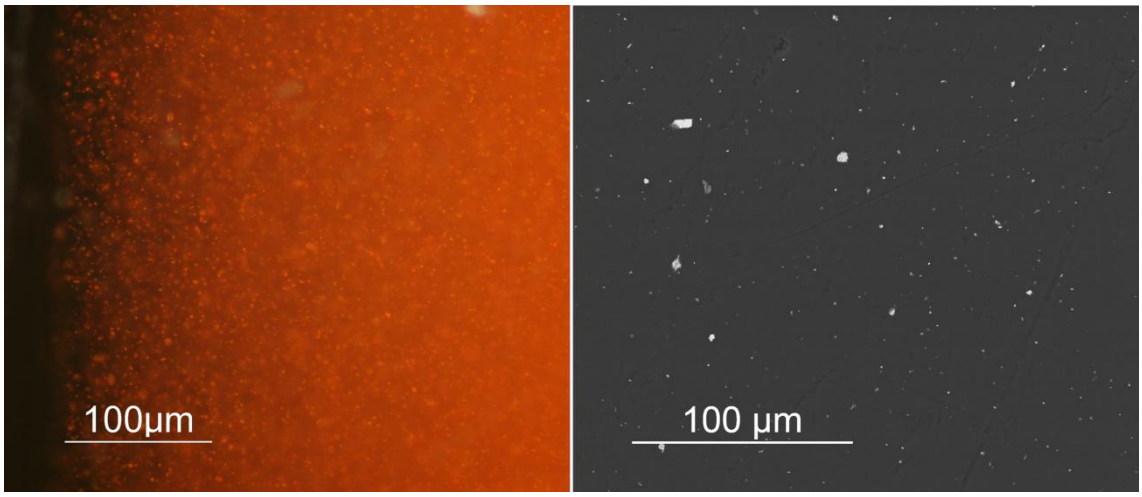


Figure 4.2: Cross-section of the red PMMA sample LC/Altuglas where pigment and filler distribution is observed. Left: optical microscope image under cross-polarised light. Right: SEM-BSE image.

Inorganic colorants and fillers in the red and nacreous samples were identified by EDXRF and µ-Raman, Table 4.3 summarises the results obtained. Barium was identified in all samples except Paraglas_6700 and, although it was not possible to confirm by µFTIR or µ-Raman, its presence is probably associated with the use of barium sulphate ($BaSO_4$) as filler, since the spatial correlation between barium and sulphur was observed with SEM-EDS elemental analysis.

In most red samples, colour is provided by cadmium pigments, cadmium sulphoselenide, Cd(S,Se), and probably cadmium mercury sulphide, Cd,Hg(S), which are common industrial inorganic pigments for colouring plastics. However, in one sample, the colouring agent is probably organic, since the only element detected by EDXRF was barium and the sample exhibited a strong homogenous fluorescence under UV light in the optical microscope.

Table 4.3: Summary of the analytical results for the red coloured samples

Sample	FTIR	EDXRF	Raman	SEM-EDS
LC/Altuglas	PMMA	Se, Cd, Ba, Sr	Cd(S,Se)	S, Se, Sr, Cd, Ba
P.Sado_9081	PMMA	Se, Cd, Ba	Cd(S,Se)	S, Se, Cd, Ba
P.Sado_9082	PMMA	Cd, Hg, Ba	-	-
Paraglas_6470	PMMA	Ba, (Ti?)	TiO_2	-
Paraglas_6500	PMMA	Se, Cd, Ba	Cd(S,Se)	S, Se, Cd, Ba
Paraglas_6700	PMMA	Ti, Cr, Fe	TiO_2	-

In the three nacreous samples, lead (Pb) was identified by EDXRF. Its presence is associated with thin hexagonal platelets, circa 10μm in diameter and less than 1μm thickness, which were seen in the optical microscope. Due to their small size, these platelets could not be identified by Raman spectroscopy, however, their shape, size, nacreous properties, and use are in accordance with descriptions found in the literature (Feller et al 1971; Corbeil and Sirois 2007) for pentalead tricarbonate dihydroxide oxide, $3PbCO_3•Pb(OH)_2•PbO$, sometimes called plumbonacrite, and most probably correspond to this pigment. The nacreous effect is obtained by reflection and scattering of light on thin multiple layers, thus, the platelets should be oriented inside the polymer matrix so that their broad faces are parallel to each other and to the surface of the plastic sheet (Buxbaum and Pfaff 2005).

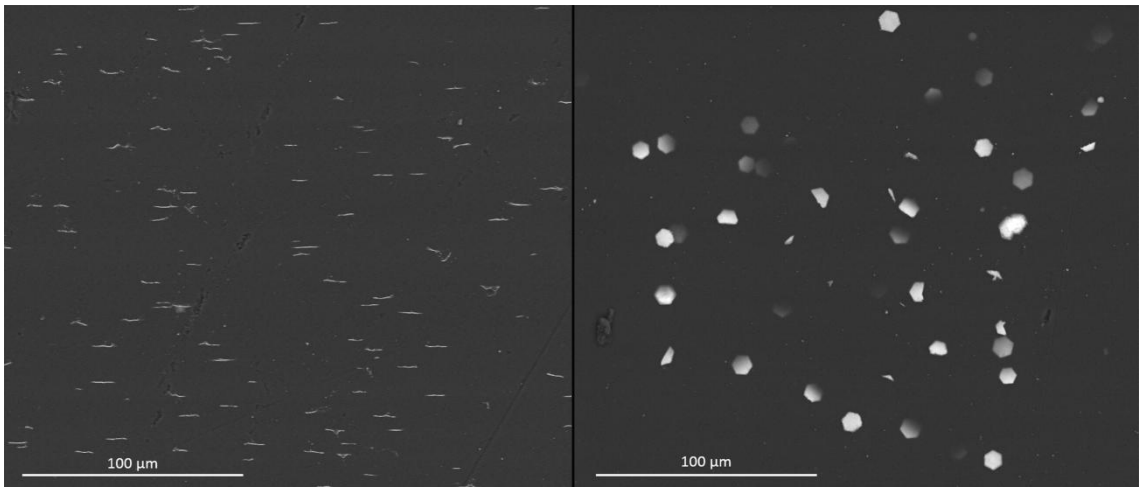


Figure 4.3: SEM-BSE images of AS_P.Sado_y.nac sample. Left: cross-section; right: top view. The hexagonal platelets are oriented parallel to each other and to the surface, providing a nacreous effect to the acrylic sheet.

In fact, this tendency was observed when analysing the samples under the optical microscope: the cross-section showed only thin short lines (a section of the hexagonal platelets) whereas in the samples prepared with a surface parallel to the surface of the sheet numerous hexagons could be observed. This effect was even more apparent when the same samples were further analysed by SEM-EDS in BSE mode (Figure 4.3).

By disturbing the alignment of the platelets during the polymerisation of the resin, after a certain viscosity had already been achieved, different effects could be obtained (Leary 1949). According to Sónia Apkan these types of sheets were produced in Plásticos do Sado with the help of a metal tool with a forked end, which would be inserted inside the mould to agitate the viscous resin in such a way that would form a pattern. The pattern became permanent through the subsequent polymerisation of the sheet in the water tank. The nacreous sheets were produced in small sizes, as squares, and were sold mainly for the production of buttons and cutlery handles (Apkan 2015). It is likely that this process was used in the nacreous sheets purchased by Ângelo de Sousa.

Transparent and red samples based on Cd(S, Se) were further analysed with the aim of understanding possible relations between production processes and sample properties. This was conducted in an exploratory approach, thus the results presented are preliminary.

Molecular weight distributions were compared in order to ascertain if a correlation could be established with the different polymerisation conditions mentioned previously. Figure 4.4 shows the chromatograms of the samples analysed. As expected, all molecular weights[13] fall in the order of millions (10^6) confirming that a casting process was used in their production (Stickler and Rhein, 1992). One interesting feature is that chromatograms from the transparent and red samples from Paraglas are almost equivalent and show low dispersity. This is in accordance with their production process; the Rostero Process, and the use of a termination agent also noted by Carvalheira (2015), which enables high control of molecular weight. The opposite is observed in the samples from Plásticos do Sado; their two chromatograms do not overlap and are broader, indicating that they have different average molecular weights and dispersity. The red sample in particular exhibits high dispersity with a considerable contribution from low molecular weight polymer chains. This is in accordance with the information from Apkan regarding the use of lower quality material in the production of opaque sheets. The differences with samples from Plásticos do Sado in comparison to Paraglas

[13] M_w and M_w/M_n are not presented since more measurements are necessary to guarantee accurate values.

are possibly due to the lack of control during polymerisation and particularly the lack of the post-polymerisation step in the processes used by Plásticos do Sado. The presence of low molecular weight polymer chains may also be related to the beginning of degradation through chain scission (Fox 1967, Bracci 2003). The more rudimentary technology involved in Plásticos do Sado process and their use of recycled raw material for the production of MMA (particularly if the purification step for the monomer was not carefully controlled), may have favoured the presence of impurities which could in turn be responsible for chromophore groups that could initiate the photodegradation process. The Plexiglas® sample from Lourdes Castro (dating from the 1960s) displays the highest molecular weight and the lowest dispersity when compared to the Altuglas sample from the same period, and the more recent ones from Paraglas and Plásticos do Sado.

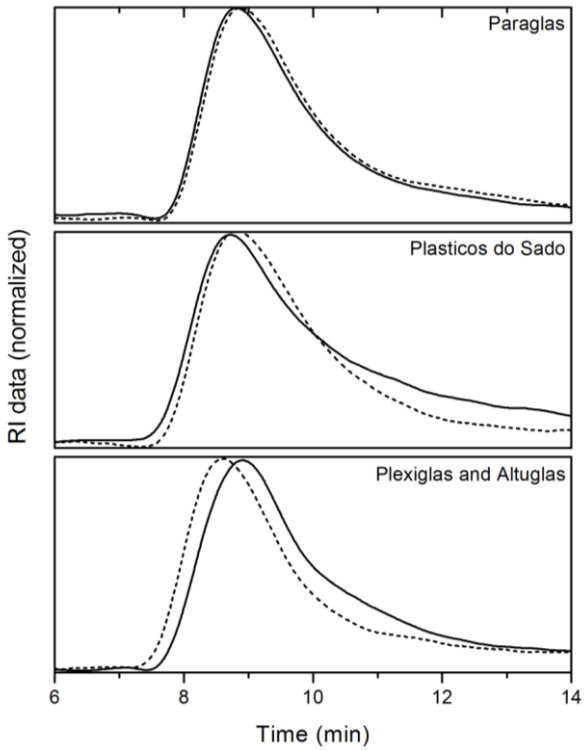


Figure 4.4: SEC chromatograms of the PMMA sheets. Dashed line: transparent samples. Solid line: opaque red samples.

Concerning TGA results, transparent and red samples were compared separately, but in both groups the same trend is observed (Figure 4.5). For Paraglas samples the onset degradation temperature is slightly higher than for all of the others. Both samples from Plásticos do Sado are less stable, beginning their thermal degradation at

temperatures ca. 100°C lower than the others. This is in accordance with the lower molecular weight and broader distribution observed by SEC.

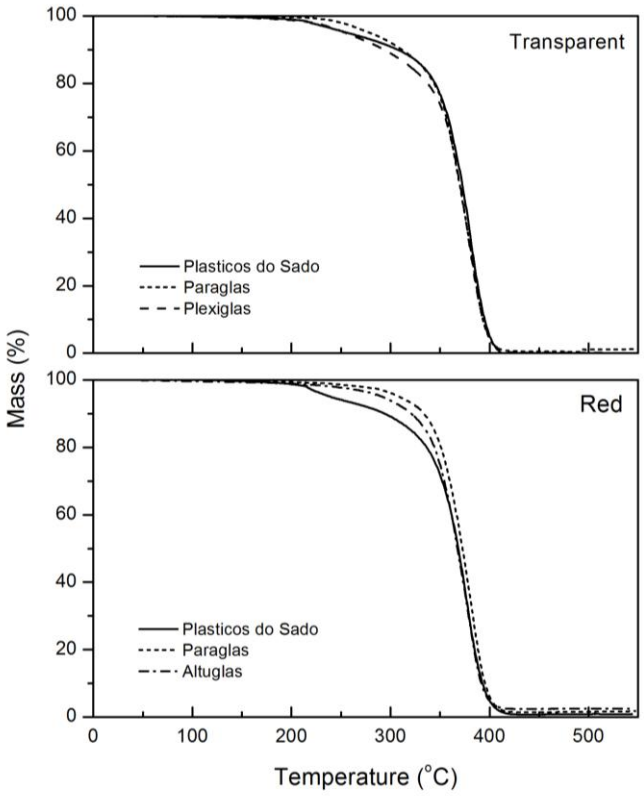


Figure 4.5: Thermograms of PMMA transparent and red sheets of Plásticos do Sado, Paraglas, Plexiglas and Altuglas.

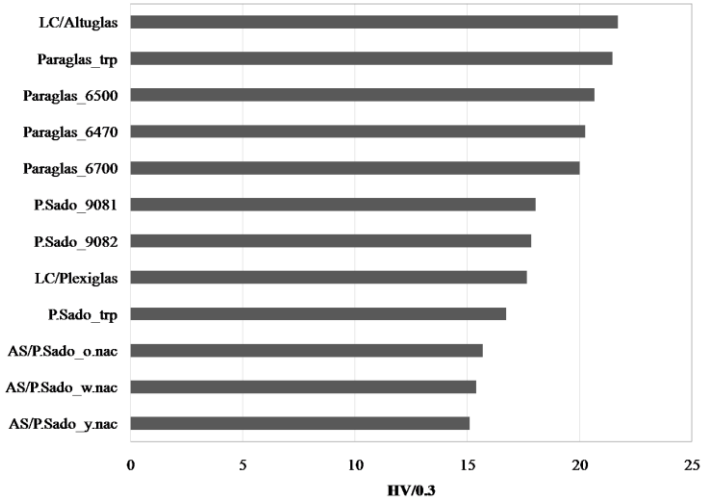


Figure 4.6: Vickers hardness of PMMA samples using a 0.3 kgf test force.

Physical testing was performed by measuring Vickers hardness by micro-indentation. This technique was chosen because it only required a small sample and no further preparation. The red sample from Lourdes Castro, LC/Altuglas shows a higher value of Vickers hardness, and the transparent LC/Plexiglas is slightly softer. But the most significant result comes from looking at all samples. If they are all ordered by hardness, two groups are formed regardless of their colour or age: the hardest are from Paraglas and the least hard are from Plásticos do Sado (including the nacreous samples), Figure 4.6. In the case of Plásticos do Sado this is likely related to the lack of a postpolymerisation step, which gives rise to less homogeneous and lower molecular weight chains.

4.5 Conclusions

With this study an important contribution to the history of the plastics industry in Portugal was achieved. It is now clear that acrylic sheet was produced in Portugal between 1955 and 2009 and apparently at least four companies were in operation during the 1960s, including Plásticos do Sado. The latter most likely produced the acrylic sheets used by Ângelo de Sousa in his sculptures. It has also become clear that the production process used by Plásticos do Sado was less controlled than those used by the other companies studied. Whether this will significantly influence the long-term ageing of this material remains to be investigated in future work. However, the preliminary results obtained suggest that there is in fact a connection between particular aspects in the production technique and the molecular and physical properties of the material. This emphasizes the importance of characterising the material beyond polymer identification to understand the properties and ageing behaviour of a plastic object.

This is an Accepted Manuscript of an article published by MDPI:

S. Babo, J.L. Ferreira, A.M. Ramos, A. Micheluz, M. Pamplona, M.H. Casimiro, L.M. Ferreira, and M.J. Melo.
'Characterization and Long-Term Stability of Historical PMMA: Impact of Additives and Acrylic Sheet Industrial Production Processes'.
Polymers, 2020, 12(10): 2198.
https://doi.org/10.3390/polym12102198

5 Characterization and study of the long-term stability of historical acrylic sheets: impact of additives and industrial production processes.

Abstract

This work aims at understanding the influence of the production processes and materials in the properties and long-term behaviour of acrylic sheet, i.e.,poly(methyl methacrylate) (PMMA), a material generally considered very stable in museum collections. A comparative study was conducted in samples from cast acrylic sheets produced in the early 2000s, from which manufacturing details were known, and samples provided by the artist Lourdes Castro from acrylic sheets she had bought in the 1960s. Transparent and red opaque cast acrylic samples, containing cadmium red pigment, were used. All samples were artificially aged in a solarbox with irradiation $\lambda >$ 300 nm for a total period of 8000 h, and alterations were followed by a multi-analytical approach which included Raman, infrared (FTIR-ATR) and UV-Vis spectroscopies; gravimetry; size exclusion chromatography (SEC); thermogravimetry (TGA); micro-indentation; colorimetry; and optical microscopy. Not all cast PMMA sheets presented similar stabilities. We have concluded that the production processes (which may include the polymerization conditions, the organic additives and the origin of the monomer) play a more important role in the properties and long-term behaviour of these acrylic sheets than the presence of cadmium red and/or the age of the material.

5.1 Introduction

Acrylic sheet, which consists of almost pure poly(methyl methacrylate) (PMMA), was developed industrially in the 1930s as the first "organic glass" (Aftalion 2001, 151; Painter and Coleman 2009, 323). Its remarkable optical properties, stiffness, light weight, mechanical and weathering resistance, ability to be easily thermoformed, and its capacity to be produced in different colors and transparency/opacity levels, made this material suitable for countless applications, such as airplane cockpits, architectural roofing systems, illuminated signs, sanitary furniture, or sophisticated design objects, just to name a few examples (Tilley 1994; Altulor 1998).

The properties of PMMA sheets were also attractive to artists, who began to incorporate this material in their artistic production, acquiring it from international recognized industrial companies or from micro-size enterprises, especially from the 1960s onwards when plastics in general became more available and widely spread in society (Restany 1973; Waentig 2008). In the conservation field, PMMA is considered a very stable plastic in opposition to other more instable plastics such as cellulose acetate, cellulose nitrate, plasticized poly(vinyl chloride) (PVC), and polyurethane (Shashoua 2008; Keneghan and Quye 1999; Ferreira et al. 2010; Bussiere et al. 2014). However, there is still much to be known on how intrinsic factors, related with the materials and methods used by different producers, may impact on PMMA stability and lifetime. Following our previous research (Babo et al. 2017) our aim was to understand which intrinsic factors – e.g., the temperature and completeness of the polymerization process; the origin of the monomer; and the presence of additives, including an inorganic colorant (cadmium red) – may have a significant influence on the properties and susceptibility of PMMA sheets to photooxidation.

The main ageing mechanism of PMMA, photooxidation, has been extensively studied (Fox et al. 1963; Fox 1967; Abouelezz and Waters 1978; Abouelezz and Waters 1979; Gupta et al. 1980; Torikai et al. 1990; Siampiringue et al. 1991; Mitsuoka et al. 1993; Rabek 1995, 135-146; Melo et al. 1999; Kaczmarek et al. 2000; Ferreira 2011). The photodegradation mechanism of methacrylic and acrylic polymers has been followed by size exclusion chromatography and a distinction in behaviour has been observed (Melo et al. 1999; Chiantore et al. 2000; Bracci and Melo 2003). In both, scission and crosslinking are present, with scission being the dominant mechanism in acrylics, whereas in methacrylics crosslinking may compete depending on the volume of the side group, and it is therefore residual in PMMA (the methacrylic with the smallest side group, a methyl). Films and sheets of PMMA should absorb bellow 260 nm (Foxet al. 1963; Abouelezz and Waters 1978; Abouelezz and Waters 1979; Gupta et

al. 1980; Torikai et al. 1990; Siampiringue et al. 1991; Mitsuoka et al. 1993); however, chromophores such as hydroperoxide groups are usually present in the polymer matrix as consequence of synthesis and processing, which may absorb radiation at wavelengths higher than the polymer and initiate photodegradation reactions (Lemaire et al. 1996). The singularity of the stability of PMMA may be further explained by the fact that, to obtain the excellent optical properties typical of an acrylic sheet, the level of impurities must be extremely low (Davisand Sims 1983, 215-219). Moreover, these impurities, or other chromophore species responsible for the initiation of photooxidation processes, do not have a catalytic effect. According to Sirampiguer and co-workers (Siampiringue et al. 1991), alcoholic groups are formed as PMMA photooxidation products. These authors also suggested that in PMMA cast sheets of 3-6 mm thickness, the photooxidation would take place only in a superficial layer of ca 500 μm, because of the low permeability of oxygen in PMMA (Siampiringue et al. 1991).

Most of the photodegradation studies on PMMA have been performed on pure polymer films prepared in laboratory, sometimes with controlled addition of other compounds/additives, and typically with radiation at $\lambda < 300$ nm to accelerate degradation. Fewer studies (Siampiringue et al. 1991; Dickens et al. 1984; Ferreira et al. 2011; Miller et al. 2017) have been conducted with commercial PMMA sheets and with radiations more similar to what an artwork may be exposed in real life.

It is also known that pigments can play a major role in the stability of a polymer matrix. Regarding photostability, pigments can either induce a protective effect by absorbing and/or screening UV light, or catalyze/accelerate the photochemical breakdown of the polymer by being photoactive (Allen 1994; Ferreira et al. 2010). Cadmium reds consist of cadmium sulphide co-precipitated with selenium, ($CdS_{1-x}Se_x$) (Charvat 2004; Buxbaum and Pfaff 2005, 121-123). In the coloring of plastics, cadmium pigments are commonly used together with $BaSO_4$ in the form of lithopones, allowing the reduction of costs while maintaining good color values and stability (Charvat 2004; Eastaugh et al. 2004, 70-72). In a recent work, the identification of this family of pigments in historical PMMA samples has been investigated (Angelin et al. 2020), but to the best of our knowledge, studies that correlate their presence with the photostability of PMMA are still missing.

5.1.1 Industrial Production Processes of Cast Sheets

PMMA sheets may be cast or extruded. Extruded sheets only became available in the late 1970s (Tiley 1994; Cholod and Miller 1992) and are of poorer quality than cast sheets (Cholod and Miller 1992). The process of producing cast sheets is well described in several references (Stickler and Rhein 1992; Altulor 1998; Slone 2004) and consists

basically in introducing monomer (or a pre-polymerized syrup of monomer), initiator, and other additives into glass molds. These are formed by two parallel polished glass plates, which are held apart by a flexible gasket and clamps. The filled molds are heated at controlled temperatures for polymerization of the methyl methacrylate (MMA). The duration of the process may vary from few hours to days depending on the sheet thickness and the technology used.

In our previous work (Babo et al. 2017), detailed information was collected about the production process of acrylic sheet in two different companies operating in Portugal between 1960s–2000s, Plásticos do Sado and Paraglas. These two companies produced exclusively cast PMMA sheets through radical initiated bulk polymerization. Even so, different methods were followed at each plant, which may have influenced the properties of the final material. The main aspects are summarized in Table 5.1.

Table 5.1: Main characteristics of the production of poly(methyl methacrylate) (PMMA) sheets in the two different plants (adapted from Babo et al. 2017).

	Plásticos do Sado	**Paraglas**
Monomer	Produced by the company through chemical recycling (depolymerization by pyrolysis) of acrylic scrap[a]	Pure monomer acquired from Degussa (Germany) or Repsol (Spain)
Solution poured into the molds	Pre-polymerized syrup (degree of polymerization empirically tested, prepared by heating monomer with initiator AIBN) + colorantes and additives	Monomer + initiator (AIBN) + colorants and additives
Polymerization	Polymerization in water tanks. Molds placed vertically in water tanks and heated to 50–60°C	Rostero process[b]. Polymerization in a chamber with pressure and temperature control. Molds held vertically between metallic plates and heated to 75–80 °C
	Polymerization completed in water tanks at higher temperature (but <100°C)	Polymerization completed in the chamber at 120 °C (post-polymerization)

[a] From cutting remains or end of life material. Several of the recycling steps were controlled visually, based on the empirical knowledge of the workers.

[b] Rossetti and Haberl 1967; Rossetti 1970; Rossetti 1973.

Comparing the processes used by the two companies, the one used by Paraglas most probably presented advantages concerning the final quality of the material produced, namely:

1. Use of pure monomer, assuring less contaminants in the final product. Even though feedstock recycling of PMMA through pyrolysis is a well-established method to produce MMA (Sasse and Emig 1998; Kaminsky and Eger 2001), it is known that the purity of the material obtained may be affected by the

presence of water and the composition of the scrap used for recycling (Brand 1995).Therefore, acrylic produced from it may present inferior properties compared to that prepared from neat MMA (Achilias 2007; Godiya et al. 2019).

2. Better control of the uniformity of the sheets thickness, as the glass molds were hold against rigid metal surfaces.
3. Post-polymerization at 120 °C. It is known that in the first step of polymerization conversion only reaches 80% to 90% because glasslike solidification of the reaction mixture occurs, preventing higher conversion values. To assure full transformation of the monomer into PMMA, it is necessary to raise the temperature above the glass transition temperature (Tg) of PMMA, to 120 °C (Stickler and Rhein 1992).

Differences in the molecular and physical properties between PMMA sheets produced by these two companies have been revealed for the first time by our preliminary studies (Babo et al. 2017). In the present work, this research is continued by further exploring the characterization of the samples, which includes identification of the additives, and by conducting an accelerated ageing experiment in order to investigate the impact of the differences found on their long-term stability. Samples from transparent and red acrylic sheets produced by the two Portuguese companies (no longer operating but from which manufacturing details are known) and samples from PMMA sheets provided by the artist Lourdes Castro (Plexiglas® and Altuglas®) were used.Lourdes Castro (b. 1930) is a Portuguese artist, who explored the possibilities given by acrylic sheet in her artworks between 1964 and 1968, while working in Paris (Restany 1973; Castro and Zimbro 1992). The artist refers to the material she used as "plexiglas"[14] (one of the most famous names by which cast PMMA sheet was commercialized) even though she has used both Plexiglas® and Altuglas®, which she believed were the best quality acrylic sheets she could buy (Ferreira 2011). Even though production details about Lourdes Castro's PMMA samples were unknown and these samples had already more than 50 years of natural ageing, they were closer to real cases in Museums and we expected to gain more knowledge about them by comparison with the Portuguese ones. Therefore, all samples were subjected to irradiation $\lambda > 300$ nm during 8000 h. Long periods of artificial ageing are especially important in the conservation field, since artworks are expected to last for centuries. Alterations on the

[14] Plexiglas® was the name of the material produced by the German company Röhm und Haas, but it was also used for the material produced in France by Alshtom/Altulor until 1962, through an agreement with the German company. It was only in 1962 that PMMA sheets produced by Altulor started to be named Altuglas® and to compete in the market with the German Plexiglas® (Leclerc 1961) which may explain the preponderance of the name

samples were followed by a multi-analyical approach, which included gravimetry; Raman, infrared (FTIR-ATR) and ultraviolet and visible (UV-Vis) spectroscopies; size exclusion chromatography (SEC); thermogravimetry (TGA); micro-indentation; colorimetry; and optical microscopy. Results are presented and discussed, attempting to correlate the different behaviours observed with the differences in their compositions and industrial production processes used. As it will be shown in this work, not all the cast acrylic sheets are alike and present the same stability.

5.2 Materials and Methods

5.2.1 Samples

Samples from six different cast acrylic sheets were used in this study (Table 5.2). Pieces of transparent and red acrylic were kindly provided by Lourdes Castro and, according to the artist, both are dated from the 1960s and identified as Plexiglas and Altuglas, respectively. Transparent sheets and red samples from color swatches, dated from 2000s and produced by Plásticos do Sado and Paraglas, were selected from the material archive of the Conservation and Restoration Department FCTNOVA and used also in this study for comparison. Selection of the two red samples from the color swatches was based on similarity of chemical composition with the one provided by Lourdes Castro (Babo et al. 2015). The Plásticos do Sado and Paraglas samples were fundamental for this research because production details were known based on our previous work as described in the Introduction above.

Samples of 15 × 15mm^2 and 5× 5mm^2 were cut from the different PMMA sheets by a 3D carving machine (Carvey® by Inventables) with a 300W DC spindle of 12,000 rpm and 1/16" solid carbide bit, using the following cut settings: 1219.2mm/min feed rate, 228.6 mm/min, and 0.5 mm of depth per pass. All samples were cleaned from dust and grease from handling in an agitated bath at room temperature of a mixture of 1% neutral detergent (Neutracon®) in distilled water; followed by rinsing with at least 3 agitated baths of distilled water. Excess water was removed with absorbent paper and samples were left to dry in a desiccator with silica gel.

Table 5.2: Identification codes of the test samples and corresponding details.

Code	Image[a]	Producer	Date of Production	Description	Colorants[c]	Thickness (mm)	Notes
TPS		Plásticos do Sado(PT)	2000s	ColorlessTransparent	n.a.	3.12 ± 0.12	From a sheet fragment with protection film.
RPS				RedOpaque	Cd(S,Se)	2.88 ± 0.01	From a color swatch. One small piece.
TPA		Paraglas (PT)		ColorlessTransparent	n.a.	3.57 ± 0.10	From a sheet fragment with protection film.
RPA				RedOpaque	Cd(S,Se)	2.87 ± 0.01	From a color swatch. One small piece.
TPL		Plexiglas (DE?)[b]	1960s[b]	ColorlessTransparent	n.a.	4.20 ± 0.12	From a sheet fragment with protection paper.
RAL		Altuglas (FR)[b]		RedOpaque	Cd(S,Se)	2.80 ± 0.02	

[a] Photographs taken on top of a black paper;

[b] Samples provided by Lourdes Castro; date and brand were indicated by the artist; [c] Identification by XRF, SEM-EDS and Raman (Babo et al. 2017).

5.2.2 Artificial Ageing and Characterization Procedure

To compare the behaviour of the different PMMAs under study, samples were artificially aged in a Solarbox 3000e accelerated ageing apparatus (CO.FO.ME.GRA) equipped with a Xenon-arc light source filtered to $\lambda > 300$ nm, with constant irradiation of 800 W/m^2 and black standard temperature varying between 60 to 100 °C (air temperature measured inside the chamber <40 °C), for a maximum period of 8000 h (total irradiance = 22943 MJ/m^2). The UV-Vis transmission spectrum of the filter used in the solarbox is presented in Appendix III. Samples were analyzed before irradiation and after 250, 500, 1000, 2000, 4000, 6000 and 8000 h. The 15 mm side samples (in triplicates of each PMMA typology, except RPS and RPA) were used for the non-destructive analysis methods (gravimetry, optical microscopy, colorimetry, infrared, Raman and UV-Vis spectroscopies) and returned to the solarbox after analysis. The series of 5mm samples were used for the destructive methods (micro-indentation, size exclusion chromatography and thermogravimetry), therefore, at each time, two samples of each PMMA type were removed from the solarbox for analyses.

5.2.3 Analytical Methods

Optical Microscopy (OM)

Optical microscopy (OM) was used to characterize visually the surfaces of the samples and detect eventual alterations. Images were acquired using a Zeiss Axioplan 2 Imageing system, equipped with halogen (HAL 100) and mercury (N HBO 103) illuminators, coupled to a Nikon DXM1200F microscope camera and using a ACT-1 control software. Microphotographs were acquired at all ageing intervals using reflected light in bright field mode, at 50× and 500× magnifications. When necessary to examine some alterations, different magnifications and illumination modes were also used, including transmitted light, dark field and cross polarizing filters. Fluorescence microscopy images were acquired with blue-violet light, using the Zeiss Filter set 05 (excitation BP 395–440 nm, beamsplitter FT 460 nm, emission LP 470 nm).

Color Measurements

Color determinations were made using a Datacolor International colorimeter (Microflash). The optical system of the measuring head uses diffuse illumination from a pulsed Xenon-arclamp over an 8 mm-diameter measuring area. The color measurements were performed using the standard illuminant D65 and the CIE 1964 standard colorimetric observer (10°) geometry. Before color determinations, calibration was performed with bright white and black standard plates. Both the equipment measuring head and the sample were positioned in a costume made positioning mask, which allowed future measurements on exactly the same area. A white base composed of several layers of lab filter paper was used for all measurements and stored in the dark while not in use. For each determination of *L*, a* and b** color coordinates, the mean value and standard deviation of three independent measurements over the same measurement area on the three sample replicates were calculated (nine readings),except for RPS and RPA which do not have replicates (three readings). Color variation in samples during artificial ageing was calculated according to the CIE 1976 (CIELAB) color difference (ΔE^*) expression (Schanda 2007, 87):

$$\Delta E_{ab}^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2},$$

in which ΔL^* is the variation in Lightness, $\Delta a^*$the variation in the red/green color coordinate, and Δb^* the variation in the blue/yellow color coordinate.

Gravimetry

Weight measurements were performed in a Sartorious CP225 D micro analytical balance. At each irradiation time, the mean value of three independent weight measurements was calculated and mass loss determined by subtracting the corresponding value obtained at $t = 0$ h. Final mass loss corresponds to the mean of the mass loss values of the three replicates for each typology (includes nine readings) converted to percentage of total initial weight. Samples were kept in a desiccator after irradiation until weight measurements were performed.

UV-Vis Spectroscopy

Ultra-violet and Visible spectroscopy was carried out both in transmittance and reflectance modes, given that both transparent and opaque samples were under study. Spectra obtained in transmittance mode were collected using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer, version 1.12, in a spectral range from 250–800 nm, at a scan rate of 600 nm/min, data interval of 1 nm and acquisition average time of 0.1 s. PMMA samples were placed in a specially designed holder (to ensure analysis was always performed in the same area) and analyzed in 0° angle (perpendicular to the light beam). Spectra obtained in reflectance mode were collected in a Shimadzu UV2501PC spectrophotometer equipped with an integrating sphere, in a spectral range from 240–900 nm, at very slow option scan rate, and data interval of 1nm. $BaSO_4$ was used as reference sample. All spectra were collected as absorption (Abs) spectra.

Infrared Spectroscopy in Attenuated Total Reflectance Mode (ATR-FTIR)

ATR-FTIR spectroscopy was carried out using an Agilent Handheld 4300 FTIR spectrophotometer, equipped with a ZnSe beam splitter, a Michelson interferometer and a thermoelectrically cooled DTGS detector. All spectra were acquired with a diamond ATR module, 64 scans and 4 cm^{-1} resolution. Three independent spectra were collected for each sample. All spectra are presented as acquired, without baseline corrections or other treatments except normalization to the carbonyl peak intensity, allowing a direct comparison of relative intensities to be made.

Raman Spectroscopy (μ-Raman)

Raman spectroscopy was carried out using a LabRAM 300 Horiba JobinYvon spectrometer, equipped with a He–Ne 17 mW laser operating at 632.8 nm. The system was calibrated using a silicon standard. The laser beam was focused with a 50× Olympus objective lens. The laser power at the surface of the samples was controlled with neutral density filters. Raman data analysis was performed using LabSpec 5

software. All spectra are presented as acquired without any baseline correction or other treatment except normalization.

Size Exclusion Chromatography (SEC)

Molecular weight distributions were determined with a KnauerSmartline system composed by a model 3800 autosampler, a 1000 pump, and a 2300 refractive index detector. Data was collected with DataApexClarity software, version 5.0.5.98. Separation was performed by two Waters Styragel HR 5E columns, with 7.8mm× 300 mm, and 5 µm particle size, after a Waters Styragel pre-column.Sample solutions in tetrahydrofuran (THF anhydrous >99.9%, Sigma-Aldrich) at approximately 0.15% (*w*/*v*) concentration were prepared at room temperature and filtered with 0.45 µm pore filters. Distilled THF stabilized with butyl-hidroxytoluene (BHT) was used as eluent at a flow rate of 1ml/min; the operating temperature was 30 °C. Column calibration was performed with monodispersed PMMA standards from Polymer Laboratories (M_p: 1.14 × 10^3 to 1.25 × 10^6). Molecular weight distribution values, including weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular-weight dispersity ($Đ_M$), were determined with the software DataApex Clarity, version 7.4, using the GPC analysis extension. Material for analysis was collected with a scalpel from the surface of the PMMA samples. At least two analyses, with independent sample collection and preparation, were performed to verify the consistency of the results.

Micro-Indentation

Vickers micro-hardness measurements were performed on an Indentec (Zwick/Roell) ZHµ Micro Hardness Tester. Vickers hardness (HV) is the quotient obtained by dividing the load applied by the square area of indentation, according to:

$$\mathrm{HV} = 1.854 \times \frac{F}{d^2},$$

where F is the load in kgf and d the arithmetic mean of the two diagonals in mm. In this study, the load used was 0,3 kgf and the application time was 15 s. For each sample, the values presented result from the arithmetic mean of five different HV measurements, performed at a distance >5d from each other. Due to the influence of relative humidity in the HV, samples collected at each ageing time were kept in a desiccator and measured in a row in consecutive days at the end of the experiment.

Thermal Analysis

Thermal analysis was performed by thermogravimetry (TGA). Measurements were carried out in a TGA Q500 (TA Instruments), in nitrogen atmosphere, from 25 to

500 °C, at a rate of 10 °C/min. All PMMA typologies under study were analyzed before accelerated ageing; analysis during ageing was only conducted in the transparent samples (TPS, TPA, and TPL) after 0, 500, 2000, 8000 h of irradiation. At least three TGA measurements were performed for each sample tested.

Thermodesorption-Gas Chromatography/Mass Spectrometry (TD-GC/MS)

Additive characterization was performed using a Multi shot Pyrolyzer EGA/PY-3030D (Frontier Lab.) coupled with a 7890B gas chromatograph and a 5977B MSD mass spectrometer (both Agilent Technologies). Around 200 µg of sample was added directly into a stainless steel Eco-cup sample holder (Frontier Lab). The thermodesorption was carried out from 50 (hold for 30 s) to 250 °C (hold for 3 min) with an increasing ratio of 20 °C/min and cryo-trap for the volatile focalization. GC separations were performed using a Frontier UA5 capillary column (30m–0.25F, 30 m × 250 µm × 0.25 µm, Frontier Lab.), Heliumas a carrier gas at the flow rate of 1.2 mL/min, and a split ratio of 30:1. The injector temperature was set to 300 °C. The column temperature program was set from 40 °C (hold for 2 min), increasing rate of 20 °C/min until 280 °C (hold for 15 min). The ionization mode was electron impact at 70 eV in positive mode, the transfer line at 280 °C, the ion source temperature at 230 °C and a scanning mass range of 29 to 550 m/z. MSD ChemStation (Agilent Technologies) software was used for data analysis and the compounds were identified by interpretation of their EI mass spectra and comparison to NIST MS Search 2.2 and F-Search 3.5.0 (Frontier Lab) databases.

5.3 Results and Discussion

5.3.1 Characterization of the Test Samples

Optical Microscopy and Colorimetry

Observation of the transparent samples through optical microscope (OM) showed no significant features, and the surfaces from the three different sheets seemed identical. In turn, some particularities were observed in the red samples. Figure 5.1 presents OM images of cross-sections of the three red samples. It is visible that RPS sample presents bigger pigment agglomerates than RPA or RAL, which might indicate the use of less finely grounded pigment by Plásticos do Sado. Regarding the RAL sheet, one of the surfaces of the samples presents more accumulation of pigment than the other, Figure 5.2, which might indicate that polymerization of the PMMA was conducted in

horizontal position allowing the pigment to sediment. Although in both industrial methods studied in Portugal the polymerization was mentioned to have been conducted in vertical orientation, the horizontal position was also common (Cholod and Miller 1992; Stickler and Rhein 1992; Slone 2004) and agrees with the description of the process for Altuglas® production in (Altulor 1988; Michel 2012).

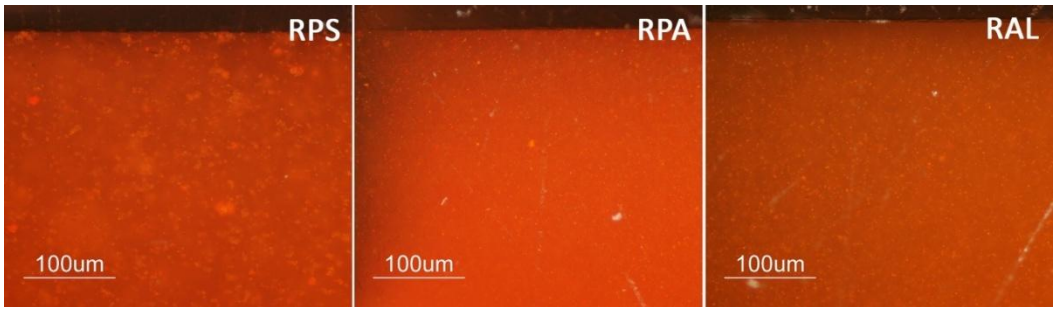


Figure 5.1: Optical microscopy (OM) images of cross-sections of the different red PMMA samples before artificial ageing. Images acquired under reflected light and cross-polarizing filters at 200× original magnification.

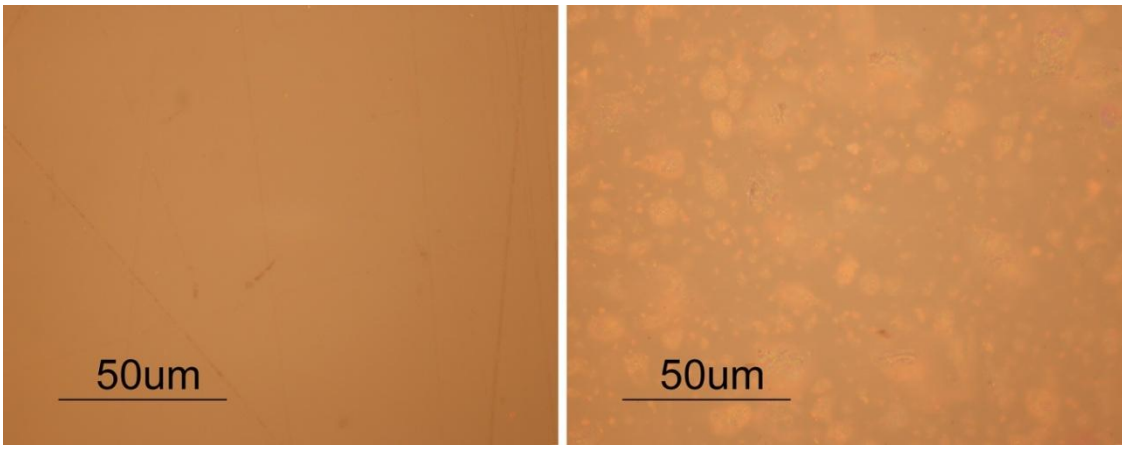


Figure 5.2: OM images of the two surfaces of RAL acquired under reflected light, bright field, at 500× original magnification. Images show that the two surfaces of the sheet are not similar, one having more accumulation of pigment agglomerates than the other. The sedimentation of the pigment might be an indication that polymerization of the PMMA sheets was conducted in horizontal position.

Table 5.3 presents the average values and respective standard deviation for colorimetric measurements (L^*, a^*, b^*) on the test samples. The values obtained for the transparent samples result from the white paper used as base during measurements, with the goal of detecting and following an eventual yellowing during the artificial ageing experience. Therefore, the lower L^* value of TPL when compared to the other transparent samples before ageing, may be attributed to the higher thickness of these samples, which results in a greater barrier for light reflection on the white paper. In turn, the lower L^* value obtained for the RPA sample reflects its visible darker color when compared with the other red samples. The higher standard deviation associated with b*

coordinate obtained for RAL samples is most probably related to the differences between top and bottom surfaces (Figure 5.2).

Table 5.3: Average values and standard deviation for color coordinates (*L**, *a**, *b**) of the test samples, before and after 8000 h artificial ageing, and respective variation.

	0 h			8000 h			Variation			
	*L**	*a**	*b**	*L**	*a**	*b**	Δ*L**	Δ*a**	Δ*b**	Δ*E**
TPS	91.16 (±0.12)	–0.25 (±0.02)	4.78 (±0.03)	89.81 (±0.17)	–0.21 (±0.02)	5.37 (±0.03)	–1.35 (±0.05)	0.04 (±0.03)	0.60 (±0.05)	1.48 (±0.03)
RPS	38.73 (±0.01)	61.33 (±0.02)	52.81 (±0.05)	40.15 (±0.01)	56.92 (±0.02)	42.19 (±0.07)	1.43 (±0.01)	–4.41 (±0.04)	–10.62 (±0.11)	11.59 (±0.11)
TPA	91.32 (±0.00)	–0.04 (±0.01)	4.14 (±0.01)	90.07 (±0.04)	–0.07 (±0.01)	4.98 (±0.01)	–1.25 (±0.05)	–0.03 (±0.02)	0.83 (±0.01)	1.51 (±0.04)
RPA	32.78 (±0.01)	56.72 (±0.01)	41.64 (±0.18)	31.93 (±0.01)	54.04 (±0.03)	40.18 (±0.17)	–0.85 (±0.02)	–2.68 (±0.04)	–1.46 (±0.12)	3.17 (±0.05)
TPL	89.75 (±0.20)	–0.30 (±0.01)	4.73 (±0.02)	87.26 (±0.21)	–0.04 (±0.02)	5.39 (±0.01)	–2.50 (±0.27)	0.26 (±0.02)	0.66 (±0.02)	2.60 (±0.25)
RAL	36.33 (±0.18)	57.74 (±0.25)	51.26 (±1.09)	39.34 (±0.04)	56.17 (±0.13)	47.28 (±0.31)	3.01 (±0.22)	–1.57 (±0.12)	–3.98 (±1.07)	5.28 (±0.77)

5.3.2 Molecular Characterization

Polymer matrixes were characterized by FTIR-ATR and Raman spectroscopies, Figure 5.3. PMMA homopolymer is identified in all samples by the strong C=O stretching absorption peak at 1723 cm^{-1} and the characteristic profiles and relative intensities of the other diagnostic peaks, namely the C–C–O stretching at 1269 and 1239cm^{-1}, C–O–C stretch at 1190 and 1143 cm^{-1}, and C–H stretching at 2995, 2951, and 2843 cm^{-1}in the FTIR-ATR spectra. In the Raman spectra, the correspondent C–H stretching vibration peaks are visible around 2996, 2949, and 2842 cm^{-1}, as well as the carbonyl stretching at 1727 cm^{-1}. The other dominant bands in the Raman spectra are the C–H bend at 1450 cm^{-1}, the C–O–C stretching at 811 cm^{-1} and C–C–O stretching at 599 cm^{-1} (Willis et al. 1969; Lipschitz 1982). No other peaks that could be attributed to additives have been detected. This was expected since additives in PMMA sheet production are normally used in small amounts (Munn 1964; Visser 1998) and therefore may be present below the detection limits of these techniques. Alterations in the typical absorptions that could be related with degradation of the polymer in the artist's samples (TPL and RAL) were also not visible.

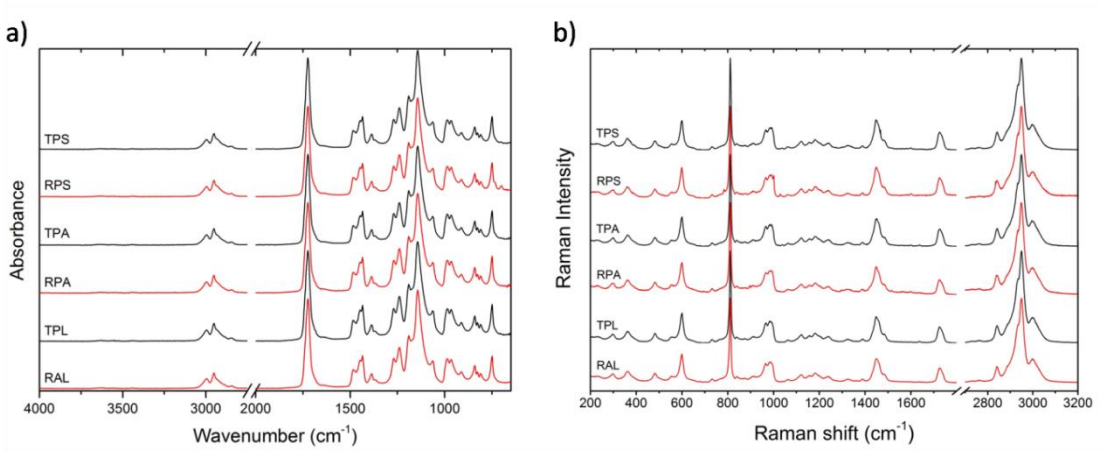


Figure 5.3: Infrared (FTIR-ATR) (**a**) and Raman (**b**) spectra of all the transparent and red samples, before artificial ageing; all spectra present a similar profile, which corresponds to PMMA homopolymer.

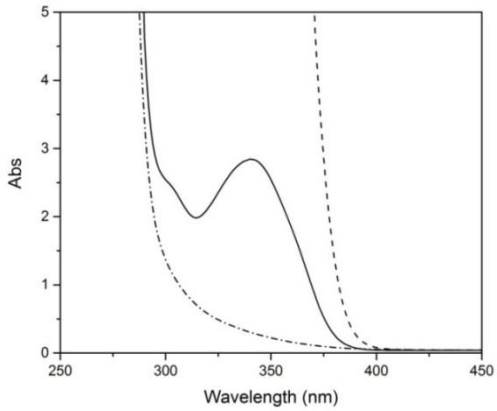


Figure 5.4: UV-Vis spectra of transparent PMMA samples; TPS (dashed line), TPA (solid line) and TPL (dash-pointed line) before artificial ageing.

Figure 5.4 presents the UV-Vis spectra of the three types of transparent samples before artificial ageing. It is known that pure PMMA absorbs mainly wavelengths <260 nm (Abouelezz and Waters 1978; Abouelezz and Waters 1979; Gupta et al. 1980; Torikai et al.1990; Siampiringue et al. 1991; Mitsuoka et al. 1993; Hsu 1999), but thick samples may present absorption until 300 nm due to the accumulation of chromophores, present in the polymer matrix as consequence of processing (Siampiringue et al. 1991). This is probably the case of TPL; however, the additional absorption at 300–400 nm observed in the UV-Vis spectra of TPS and TPA samples is most probably associated with the presence of additives. PMMA for standard use is usually modified with additives, namely UV absorbers to protect from aggressive UV radiation (Fassbender et al. 2011). The different profiles reflect different sheet formulations, which were studied further by mass spectrometry.

TD-GC/MS analysis allowed the identification of several additives such as plasticizers, UV stabilizers, and release agents on the PMMA samples; a summary of the results obtained is shown in Table 5.4.

Table 5.4: Summary of additives identified by TD-GC/MS in the PMMA samples. For the abundance calculation: Peak area MMA/peak area$_1$ < 5: xxx; 5–15: xx; 15–100: x; > 100: (x) (peak area$_1$ = peak area of the compound of interest).

Compounds	TPS	RPS	TPA	RPA	TPL	RAL
Initiators						
Azobisisobutyronitrile (AIBN)	x	x	x	x	x	x
Plasticizers						
Diethyl phthalate (DEP)	(x)	(x)	((x))	((x))	(x)	(x)
Dibutyl phthalate (DBP)	/	(x)	/	x	/	xx
Bis(2-ethylhexyl) phthalate(DEHP) = dioctyl phthalate (DOP)	xxx	xxx	(x)	/	xxx	/
Diisononyl phthalate (DINP)	/	/	x	/	/	/
UV stabilizers						
Ethyl 2-cyano-3,3-diphenylacrylate (Etocrylene)	x	/	/	/	/	/
2-(2-hydroxy-5-methylphenyl)benzotriazole (Drometrizole)	x	/	/	x	/	/
Release agents						
Palmitic acid, methyl ester	(x)	(x)	/	(x)	(x)	/
Stearic acid, methyl ester	(x)	(x)	/	(x)	(x)	((x))

xxx: High abundance; xx: Medium abundance; x: Positive presence; (x): Trace; ((x)): Ultra-trace; /: Not detected.

The initiator azobisisobutyronitrile (AIBN) was detected in all samples, which confirms the information collected regarding Plásticos do Sado and Paraglas during the historical research (Babo et al. 2017), presented in Table 5.1. Different plasticizers were detected in the samples; all were identified as phthalates, the most widely used plasticizers worldwide (Howick 1998). Bis(2-ethylhexyl) phthalate (DEHP), a structural (or constitutional) isomer of dioctyl phthalate (DOP), was detected in Plásticos do Sado samples (both TPS and RPS) and also in the artist's sample TPL. Its identification in Plásticos do Sado also agrees with the information gathered in the historical research (Babo et al. 2017). In the other artist's sample, RAL, the plasticizer identified was dibutyl phthalate (DBP). In Paraglas samples, two different plasticizers were detected: Diisononyl phthalate (DINP) in TPA, and DBP in RPA. Additionally, traces of diethyl phthalate (DEP) were detected in all samples. Although a quantitative analysis of the additives was not performed in this study, it is possible to infer from the chromatograms the relative amount of plasticizer in the different PMMA typologies by comparing the

ratio between plasticizer and MMA peaks (the main volatile). When evaluating the reference samples, it is clear that more plasticizer was used in PMMAs by Plásticos do Sado than by Paraglas. In the artist's samples, higher amount of plasticizer was detected in TPL than in RAL but this difference is not so marked. UV-stabilizers were found only in two reference PMMAs: Etocrylene (ethyl 2-cyano-3,3-diphenylacrylate) in TPS and drometrizole (2-(2-hydroxy-5-methylphenyl)benzotriazole) in TPS and RPA. The reason for using two different UV-stabilizers in the same PMMA sheet, TPS, was not clarified. Palmitic and stearic acids were detected in trace in all samples except TPA; these compounds are normally used as lubricants or release agents, facilitating the removal of PMMA sheets from the molds. The use of stearic acid as release agent in Plásticos do Sado agrees with the data collected during historical research.

Table 5.5: Evolution of weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular-weight dispersity ($Đ_M$) of the test samples during artificial ageing.

	0 h			**500 h**			**2000 h**			**4000 h**			**8000 h**		
	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_n$ ($\times 10^5$)	$Đ_M$	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_n$ ($\times 10^5$)	$Đ_M$	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_n$ ($\times 10^5$)	$Đ_M$	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_n$ ($\times 10^5$)	$Đ_M$	$\bar{M}_w$ ($\times 10^5$)	$\bar{M}_n$ ($\times 10^5$)	$Đ_M$
TPS	12.25	4.32	2.8	4.08	1.62	2.6	1.66	0.65	2.6	1.48	0.49	3.1	1.15	0.43	2.6
RPS	12.31	3.46	3.6	6.50	1.58	3.9	2.94	0.59	4.4	2.17	0.41	5.3	1.78	0.30	6.0
TPA	13.30	6.20	2.1	5.12	1.89	2.7	2.31	1.05	2.2	1.98	0.88	2.3	1.73	0.69	2.5
RPA	12.58	4.99	2.5	9.04	3.19	2.8	4.70	1.84	2.6	3.00	1.13	2.6	1.55	0.59	2.6
TPL	12.12	4.61	2.6	3.19	1.39	2.3	1.25	0.57	2.2	1.39	0.56	2.5	0.95	0.39	2.4
RAL	19.08	9.39	2.0	12.13	5.27	2.3	5.19	2.05	2.5	2.29	0.83	2.8	1.99	0.80	2.5

Molecular weight data obtained by SEC are presented in Table 5.5. In what concerns the results for the test samples before artificial ageing (0 h), all weight-average molecular weight (M_w) values fall in the order of millions (10^6) confirming that all the sheets were cast (Stickler and Rhein 1992). Comparing the samples produced by Plásticos do Sado to the ones produced by Paraglas, it is visible that the first have somewhat lower molecular weights and higher molecular-weight dispersity ($Đ_M$) values. This might be explained by two factors: The use of recycled monomer (that may introduce impurities that act as "chain-transfer agents" which short-stop the polymer growth locally and create a more irregular structure (Çetinkaya et al. 2017) and the lack of a post-polymerization step (residual monomer may also contribute to a more irregular structure). Interesting is also the difference between the two artist's samples (TPL and RAL). TPL presents similar M_w and $Đ_M$ values to the ones obtained for TPS, while RAL presents the highest molecular weight and the lower dispersity of all samples. This difference may be explained by different productions processes (unknown to the authors) as it seems to be the case with the Portuguese samples. Even so, considering

that both samples have already more than 50 years of natural ageing and that PMMA degrades mainly by chain scission (Rabek 1995), these values are an indication of the great stability of both PMMA sheets.

Mechanical Characterization (Via Vickers Hardness)

Vickers Hardness (HV) values obtained for the test samples before artificial ageing are reported in Figure 5.5. The presence of pigments and eventual fillers in the sheets does not seem to be a determinant factor for their superficial hardness, since no tendency that separates transparent from red opaque samples is observed. The same applies for the age of the sample, as the two artist's samples, both with 50–60 years old, present the highest and one of the lowest HV values, 26 for RAL and 22.6 for TPL, respectively. Again, the production method seems to be the main factor influencing the surface hardness of PMMA sheets, as both samples (transparent and red) from each Portuguese factory present similar values, being the material by Paraglas clearly harder than the one by Plásticos do Sado. What are the aspects in the production that influence the hardness? One important aspect seems to be the plasticizer. As expected, samples with more plasticizer (Table 5.4) are softer (lower HV) than the others. However, Altuglas sample (RAL) apparently has more plasticizer in its composition than the sheets produced by Paraglas (TPA and RPA) but is harder. This difference is most probably due to the higher molecular weight of RAL sample (Table 5.5). Samples with lower molecular weights present also the lower HV values. The data obtained illustrates that the surface hardness of the PMMA sheets results from the combination of these two factors, amount of added plasticizer and molecular weight.

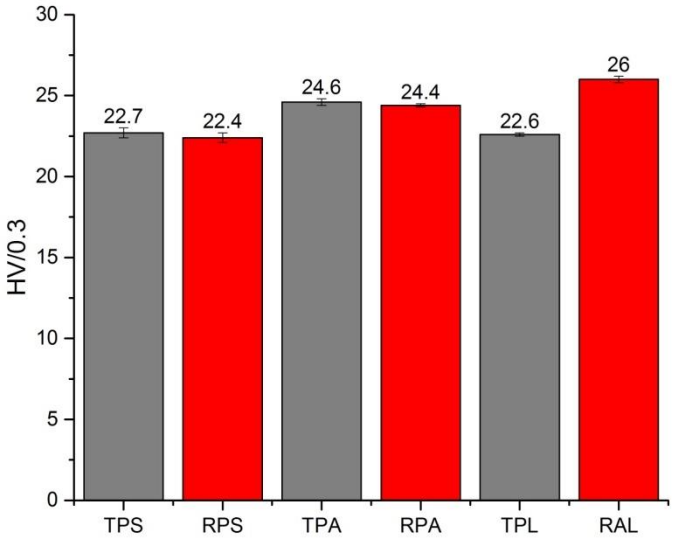


Figure 5.5: Average Vickers hardness values obtained for all PMMA samples before artificial ageing and respective error bars.

Thermal Stability

The thermogravimetric weight loss curves (TG) and the weight loss derivative curves (DTG) of both red and transparent PMMA samples are presented in Figure 5.6; the respective thermal parameters are presented in Table 5.6. All samples show a severe decrease in weight between 320–400 °C, with a maximum decomposition rate at 362–368 °C, as seen by the sharp peak on the DTG curves. This corresponds to PMMA thermal degradation via chain end initiation or a mixture of chain end with random chain scission initiation (Hollandand Hay 2002), leading to complete unzipping of the polymer chain into MMA. Because MMA volatizes, the weight drops off to 0% after this step for all the samples. Samples TPA, RPA, and RAL degrade in this single step, while samples TPS, RPS, and TPL present a previous degradation step at around 200°C.

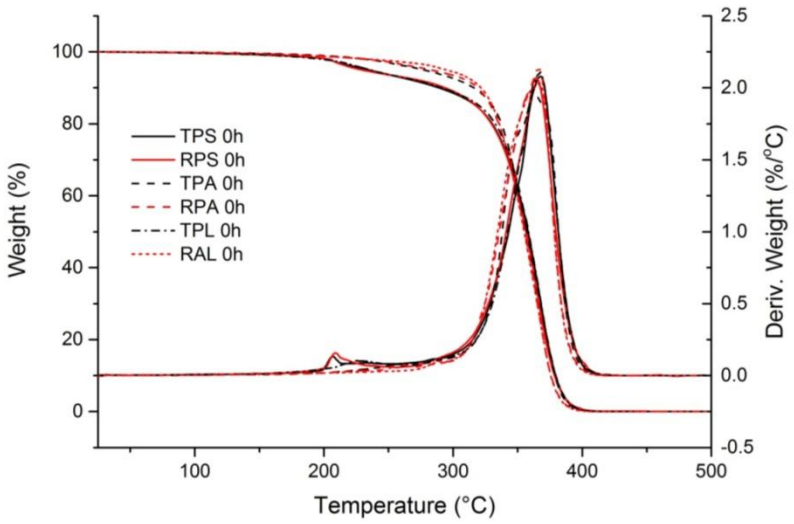


Figure 5.6: TG and DTG curves of PMMA samples before artificial ageing. Curves obtained at a heating rate of 10 °C/min, under a N_2 atmosphere.

Table 5.6: Thermal parameters obtained from the TG and DTG curves of the different PMMA samples, including onset temperature (T_0) and maximum process rate temperature (T_{max}) in °C, and respective mass losses (Δ_m) in % of original mass, for the two thermo degradation steps observed.

	Initial Step		**Main Step**	
	T_0/Δ_m	T_{max}/Δ_m	T_0/Δ_m	T_{max}/Δ_m
TPS	206/2	207/2	325/18	368/70
RPS	206/2	208/3	324/17	364/66
TPA	-	-	328/14	362/60
RPA	-	-	325/12	367/69
TPL	215/3	224/4	333/20	367/68
RAL	-	-	324/11	367/73

Thermal degradation of PMMA with more than one step has been reported by several authors (Hirata et al.1985, Kashiwagi et al. 1986; Manring 1989; Sasse and Emig 1998; Ferriol et al. 2003; Gałka et al. 2014) and the lower temperature degradation steps are attributed to internal structural defects created during polymerization such as unsaturated-end groups (vinylidene ends produced by disproportionation termination), head-to-head links (produced by recombination termination), and/or peroxides (formed when polymerization occurs in the presence of oxygen), which all have thermally labile links. Hirata and co-workers (Hirata et al.1985) have concluded that volatilization of impurities, such as unreacted initiator or residual monomer, may be responsible for weight losses at temperatures below 210° C by comparing the TG and DTG curves of a commercial PMMA sample before and after purification. In addition, it is known that the presence of additives may also influence the thermal behaviour of the samples (Gałka et al. 2014; Aouachria et al. 2014).

Several aspects may contribute to the differences in the thermal behaviour of Plásticos do Sado samples (TPS and RPS) in what relates to the first degradation step (around 206 °C). The presence of impurities may be related with the use of recycled monomer. In turn, residual monomer (if still present) is due to the lack of the post-polymerization step. Considering the composition of the samples (Table 5.4), the presence of more plasticizer (also observed in TPL) may also play a role. However, in these PMMA sheets, plasticizers are present in small quantities (not detectable by FTIR-ATR) and since the plasticizer DEHP decomposes at temperatures close to PMMA, around 323°C (Aouachriaet al. 2014), the first degradation step cannot be directly related with the volatilization of plasticizer. However, if the presence of plasticizer in the polymer matrix reduces the inter-chain interactions (Howick 1998) it may influence its thermal behaviour originating a less resistant structure. The fact that the same plasticizer, DEHP, was identified in Plásticos do Sado samples and in the artist sample TPL raises the question if not only the quantity used but also the nature of the plasticizer may have an influence on thermal degradation, but with the present data it is impossible to reach a conclusion. Nevertheless, TG curves of Plásticos do Sado reveal the presence of more structural defects in the polymer chains of these samples, which are most probably associated with the use of recycled monomer and the lower control of the polymerization. On the contrary, the use of a chain transfer/termination agent (Cacioliet al. 1984) and the performance of a post-polymerization step by Paraglas result in fewer thermally instable links in the PMMA structure, and therefore the first stage of thermal degradation of the polymer is not present. Interestingly, the presence of

Cd(S,Se) pigment does not seem to have an influence in the thermal degradation of the polymer in the reference samples.

Regarding the artist's samples, Plexiglas sample (TPL) shows a similar behaviour to Plásticos do Sado ones, while Altuglas sample (RAL) is closer to the Paraglas ones. It seems that 50 years of natural ageing did not affect the thermal stability of the samples, confirming the incredible stability of PMMA. Once more, differences observed are probably related to the presence of additives and the control of the polymerization. It is also worth notice that higher molecular weight implies less end groups potentially labile in which the chain scission can initiate; this might be contributing to the superior thermal stability of RAL compared to TPL.

Short Note Regarding the Characterization of the Artist's Samples

The differences observed between the two artist samples, TPL and RAL, were surprising. Given the common origin of Plexiglas and Altuglas in France (Leclerc 1961; Michel 2012), it was expected that the technologies used by the two companies would be similar, and consequently, the materials produced. Several aspects should be considered at this point which may contribute to these differences: (1) The two sheets have different thicknesses which may influence the properties of the material; (2) both Rohm & Haas and Altulor produced different types of PMMA cast sheets for different applications, therefore, we may not be comparing materials of similar grade; (3) the origin of the sheets is based exclusively in the notes of the artist, and thus subject to errors.

5.3.3 Assessment of Ageing Behaviour

Molecular Alterations

As expected, molecular alterations in the polymer were clearly observed by SEC analysis. The evolution of M_w, M_n, and $Đ_M$ along the artificial ageing for the test samples is presented in Table 5.5.

Regarding the reference samples, the first aspect that can be noted is that all four PMMA sheet typologies have experienced a severe decrease in their M_w (one order of magnitude), visible already after 500 h of irradiation even though radiation with $\lambda \geq 300$ nm (just in the absorption limit of PMMA) was used for artificial ageing. Furthermore, during sample preparation for SEC analysis, no gel formation was observed, which confirmed that no crosslinking took place during irradiation, in accordance with the findings of other authors (Kaczmarek et al. 2000; Bracci and Melo 2003; Ferreira 2011). These results have also confirmed that, as expected (Fox 1967; Torikai et al. 1990;

Rabek 1995, 135-146), chain scission was the main photodegradation mechanism for all PMMA samples. Regarding dispersity, no significant variations were observed along the ageing, except in RPS that presents a strong increase in the $Đ_M$ value.

For an easier comparison of the different PMMAs photo-stabilities, the number of scissions per chain was calculated and plotted against irradiation time. A linear fit was performed until 4000h and the respective parameters are presented in Figure 5.7. The values obtained are higher than in previous studies (Ferreira 2011; Ferreira et al. 2011) which may be explained by the different conditions used during the SEC analysis and in the artificial ageing, namely the higher temperature inside the ageing chamber.

With the exception of RPA, degradation appears to happen in two phases with two different rates, with a shift around 4000h, being the degradation rate higher in the first phase than in the second. Siampiringue and co-authors (1991) have followed the photooxidation of PMMA sheets at long wavelengths ($\lambda > 300$ nm) by FTIR and UV spectroscopies and concluded that photooxidation of PMMA is controlled by external chromophores (contaminants) which do not form new chromophores on the polymer structure during photooxidation and, therefore, the photo-reaction stops when the external photo-inductor is consumed. Although in the present study the photooxidation did not stop, as we continue to observe chain scissions, the slowdown of the degradation rate might be explained by the reduction/consumption of these external chromophores. Another explanation would be that the new oxidized groups formed by the chain scission would participate in other reactions and therefore not contribute significantly to new chain scissions.

Paraglas samples appear to be more resistant to photodegradation (less chain scission) than Plásticos do Sado samples. If the photostability of PMMA is controlled by the presence of contaminants, this difference between the two samples may be explained by the presence of more additives (Table 5.4) or by the use of recycled monomer (Table 5.1) by Plásticos do Sado.

When comparing samples from the same company, it is possible to observe that, with exception of RPS at 8000 h of irradiation, red opaque samples performed better than the transparent ones. This may be an indication of some protection/stabilization effect from the Cd(Se,S) pigment and/or $BaSO_4$. Cadmium red is considered a very stable pigment (Charvat 2004) but to the best of our knowledge, there are no studies that have specifically looked at the influence of this pigment on the photostability of PMMA. Pintus and co-authors (2013) have studied the influence of several inorganic pigments, including cadmium red, on the photooxidative stability of an acrylic emulsion binding medium, p(nBA/MMA), after UV ageing. Their thermal analysis results seem to show that paint samples with cadmium red exposed to UV radiation were less prone

to chain scission than the other pigmented paints tested, but they did not compare it with the binding medium alone. It is known that the photostability of a polymer system depends not only on the chemical and physical natures of the polymer and the pigment, but also on the additives present and the possible interactions between them (Allen 1994) and therefore the same pigment may have different effects in different polymeric systems (Klemchuk 1983). The change of tendency observed for the RPS sample at 4000–8000 h of irradiation must result from some not identified alteration that occurred in the polymer system during that period.

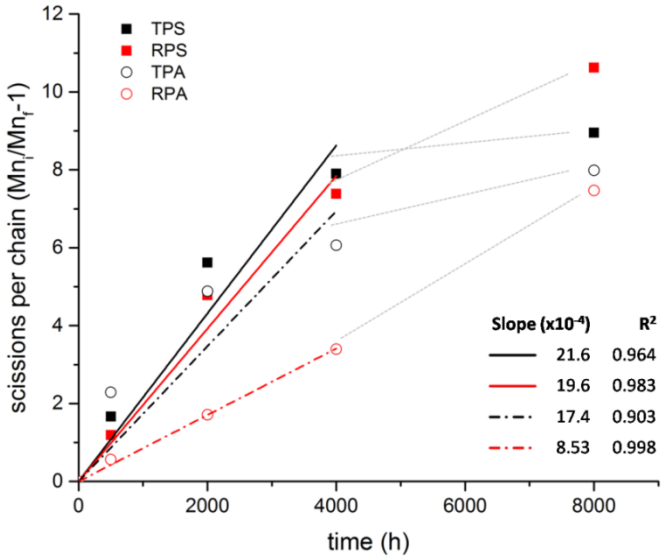


Figure 5.7: Scissions per chain of reference samples as a function of irradiation time and respective linear fit for 0–4000 h; grey lines indicate an inflection on the evolution with time.

Regarding the artist's samples, several observations can be made. First, chain scission was also the degradation mechanism observed. Second, the two samples do not present a behaviour that may be considered significantly distinctive from the reference sheets. This means that the fact that these samples have already 50 years of natural ageing, does not seem to be a significant factor in the way they have responded to artificial ageing through photodegradation. Third, in these samples, as it was also observed for the reference ones, the decrease in molecular weight was not linear, being faster in an initial phase. In RAL the shift happens around 4000 h, but in TPL it happens before, at 2000 h, when it seems to stabilize until 4000 h, then continuing again. Even so, after 8000 h, the observed number of scissions per chain was similar for the two samples, c.10.8, and very close to the highest value observed for the reference samples, 10.6 (for RPS).

Gravimetric analysis did not show significant variations that could be clearly related with the loss of volatiles as result of photooxidative degradation. After 8000 h of artificial ageing, both reference and artist's samples had lost weight, but alterations were under 0.4% of original weight (maximum value measured for the RPS sample).

Alterations were also not detected by FTIR-ATR and Raman spectroscopies in any of the samples. The shape of the peaks and their relative intensities remained unchanged, without formation of new shoulders and/or bands both in infrared and Raman spectra of the aged samples. In the one hand, since PMMA degraded through chain scission, the degradation products maintain basically the same molecular structure except additional termination groups. With the high molecular weights of cast sheet, the proportion of the additional termination groups to the main structure would be insufficient to produce visible changes in the spectra. On the other hand, because additives were used in quantities under the detection limit of these two techniques, it was impossible to follow their eventual alteration or loss during ageing.

By UV-Vis spectroscopy, however, it was possible to detect some alterations. Regarding the reference samples, alterations in the polymer matrix were not detected because the absorption by additives in the 250–400 nm interval masks the region where alterations on the PMMA could be expected (Fox 1963; Abouelezz and Waters 1979; Siampiringue et al. 1991; Kaczmarek et al. 2000). However, in TPA it was possible to follow the decrease of the band at 340 nm between 2000 and 8000 h of artificial ageing (Figure 5.8a), which indicates that the additive responsible for this absorption is being consumed/released during irradiation exposure. In TPS, the absorption in these wavelengths is so high that saturates the signal and eventual alterations cannot be detected. Alterations in the spectra of the red samples (RPA and RPS) are related with color alteration and are presented in Appendix III.

Regarding the artist's samples, a decrease in absorption in the tail at 280–400 nm in TPL is observed (Figure 5.8b). This is interesting because it is the opposite of what was observed by other authors (Siampiringue et al. 1991), which have correlated an increase in this region with the formation of photoproducts during the photooxidation of the extrinsic chromophores. Would the decrease observed in our case be related with the consumption/volatilization of those photoproducts, which were maybe formed during the natural ageing? Another possible explanation would be the loss of additives, which also absorb in this region. Interestingly, this alteration only happens in the first 2000 h, after that, between 4000 and 8000 h, the absorption is stabilized, which means that whatever was being consumed has disappeared.

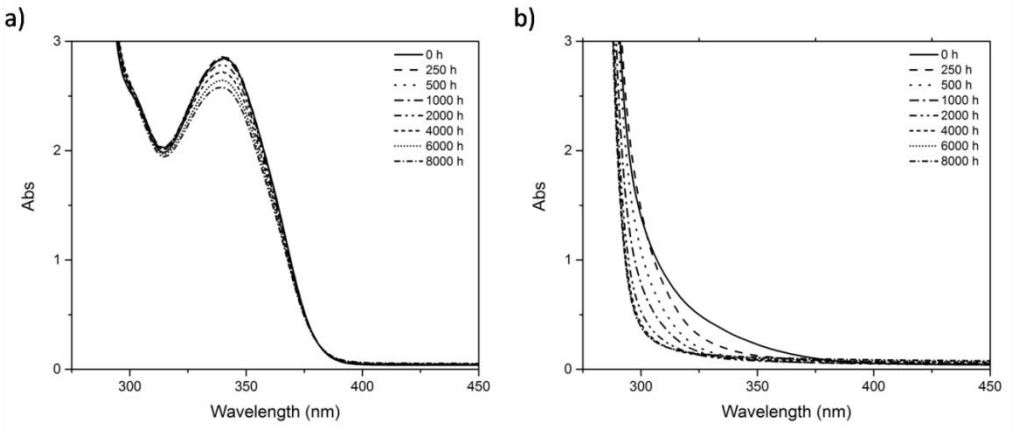


Figure 5.8: Absorption spectra of:(**a**) Reference sample TPA and (**b**) artist sample TPL, during artificial ageing.

Visual Alterations

Alterations on the test samples were also followed by colorimetry and results are presented in Table 5.3. For the reference transparent samples, ΔE^* values after 8000 h of artificial ageing are around 1.5 for both TPS and TPA, which is a variation under the JND (just noticeable difference) limit of 2.3 (Mokrzycki and Tatol 2012). However, for artist sample TPL, a ΔE^* value of 2.6 was calculated, which is above the JND and reflects mainly a decrease in the L^* coordinate. This higher ΔL^* value is probably due to its greater thickness and its ageing. Variations in red samples are more significant, especially in RPS samples with a $\Delta E^* = 11.59$. This value reflects mainly a variation on the b^* axis towards a less saturated color. Even so, it is possible to confirm the excellent lightfastness of the cadmium red pigment after such a long period of irradiation. The red artist sample, RAL, presents a variation higher than what was observed for the reference sample RPA but half of the alteration on RPS. Apparently, the 50 years of natural ageing of the artist's sample did not have a negative effect on its ageing performance, in what concerns the visual parameters observed. More data regarding color alteration in red samples is reported in Appendix III.

In addition, alterations on the samples were followed by OM by photographing the same areas of the samples along the ageing experience.

As observed by the other techniques, results show differences in the photostability of the reference samples from Plásticos do Sado and Paraglas.

In RPS, the formation of several bubble like features in the interior of the sample became evident after 2000 h of irradiation. These features, probably formed by volatile photodegradation products, have enlarged and/or have migrated to the surface afterwards, as visible in Figure 5.9. The same phenomena seemed to have started in the

TPS samples after 6000 h, but in a much minor degree. This was not observed in the Paraglas samples.

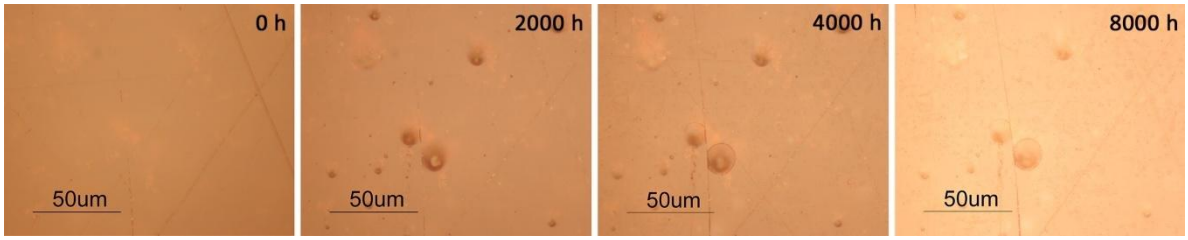


Figure 5.9: OM images of the surface of an RPS sample during artificial ageing; acquired under reflected light and in bright-field mode.

Another important aspect was the development of auto-fluorescence in the transparent samples during artificial ageing. Auto-fluorescence was observed when samples were illuminated with blue-violet light (λ = 395–440 nm), Figure 5.10. Studies that use fluorescence microscopy as a tool to follow polymer degradation are scarce (França de Sá et al. 2017) and none was found that specifically follows PMMA photodegradation. The development of fluorescence in artificially aged PMMA samples was detected by fluorescence spectroscopy by Dickens and co-workers (1984), with a maximum excitation at ~375 nm and emission at 480 nm, attributed by the authors to the formation of carbonyl groups in α-diketones and α,β unsaturated aldehydes. Other authors (Siampiringue et al. 1991) have observed an increase in the absorption spectra between 280–500 nm in commercial acrylic sheets artificially aged; the absorption at λ > 400 nm was related with the photoproducts that resulted from photooxidation of extrinsic chromophore contaminants in the polymer matrix. Probably similar photoproducts are responsible for the observed fluorescence in the samples within the present study. This phenomenon is more pronounced in the TPS samples, which indicates that this sheet is more prone to photooxidation, even if only by the extrinsic chromophores. This agrees with the results obtained with the other techniques.

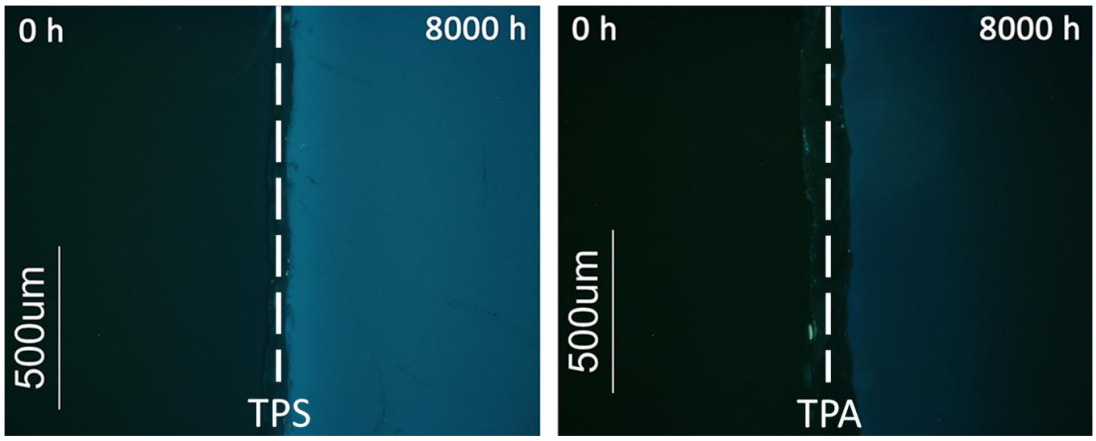


Figure 5.10: Fluorescence microscopy images under blue-violet light of TPS and TPAsurfaces.A non-aged sample (0 h) and an artificial aged sample (8000 h) of each PMMA typology were photographed side-by-side. Both PMMA sheets presented no fluorescence before artificial ageing (dark surfaces at 0 h); TPS developed more fluorescence (lighter blue under radiation) than TPA during ageing.

Observation by OM of the artist's PMMA samples could only detect alterations on TPL. After 6000 h of irradiation, small features seem to have started to form in the interior of the sample with a similar appearance and degree to what was observed on TPS after the same period of irradiation. Additionally, a micro-crack was observed on the top TPL surface and several on the bottom. There was not a significant development of auto-fluorescence. In RAL no alterations were observed after 8000 h of artificial ageing.

Mechanical Alterations (Via Vickers Hardness)

Figure 5.11a shows the variation of HV in percentage versus irradiation time, for both transparent and red reference samples. The first aspect worth notice is the increase in surface hardness with artificial ageing in all four samples. This is curious since SEC analysis has shown a decrease in molecular weight as result of chain scission, expected to correspond to a decrease of the mechanical strength. A similar increase in surface hardness (in nano-scale) was observed by other authors (Kaczmarek and Gałka 2011) for PMMA exposed to UV radiation, who have related this behaviour with a relaxation process leading to a more compact reorganization of the macromolecules of the top layer. Another factor that may be responsible for the increase in hardness in the samples under study, could be the loss (or further reactions) of plasticizers at the surface level. This would explain why Plásticos do Sado samples, which have more plasticizer (see Table 5.4), present a stronger increase in surface hardness than the ones by Paraglas. Another interesting aspect is that apparently, in both brands, red samples seem to have suffered less superficial alterations than the transparent ones. This tendency was also

partially observed for the molecular weight alteration, reinforcing that the presence of the red cadmium pigment and/or the filler might be having a protection role in the system against photooxidation.

In Figure 5.11b it is possible to follow the variation of the surface hardness of the artist's samples along the artificial ageing. As can be observed, the two samples show very different behaviours. While in RAL the surface hardness is kept almost stable during artificial ageing (variation is less than 2 %), in TPL the surface hardness is increasing continuously. It seems that after 8000 h of ageing, this already naturally aged sample is still in a process of surface reorganization. Several tentative explanations of this phenomenon could be discussed; one could be related with the loss of plasticizers, which in this thicker sample may take longer. Both behaviours are different from what was observed for the reference samples, in which after an initial period of increase in surface hardness, the samples seemed to stabilize.

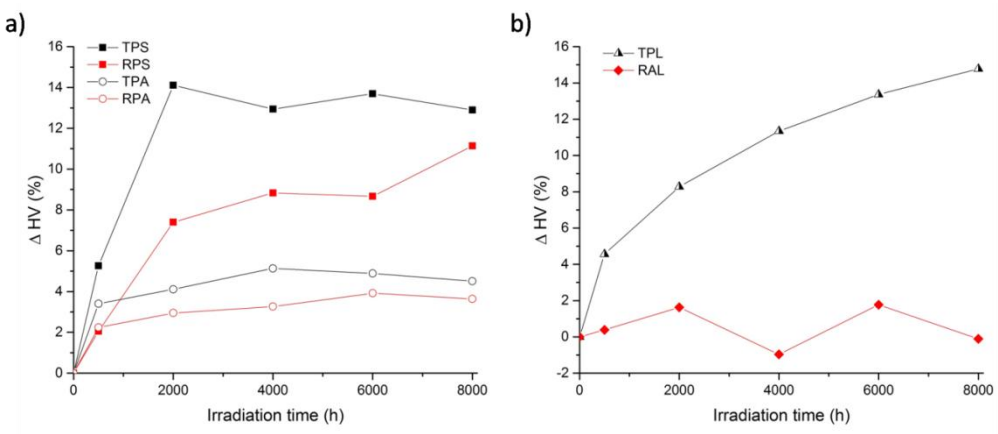


Figure 5.11: Vickers hardness values variation versus irradiation time for: (**a**) Reference samples (TPS, RPS, TPA, and RPA); and (**b**) artist's samples (TPL and RAL).

Alterations on Thermal Stability

In Figure 5.12 are presented the TG and DTG curves of the transparent samples after different irradiation times. A common feature in both reference samples (TPS and TPA) is that, with ageing, degradation starts at lower temperatures, even though the temperature of maximum decomposition rate remains the same. This shift for lower temperatures reflects the presence of more thermally labile links, which are formed during the photooxidation reactions, in particular as result of chain scission.

As observed for the reference samples, also the artist's sample TPL shows an increase of volatiles at lower temperatures with artificial ageing. But even though the

thermogram of the sample before ageing was similar to the reference sample TPS, in this case, a shift to temperatures lower than 200 °C was not observed.

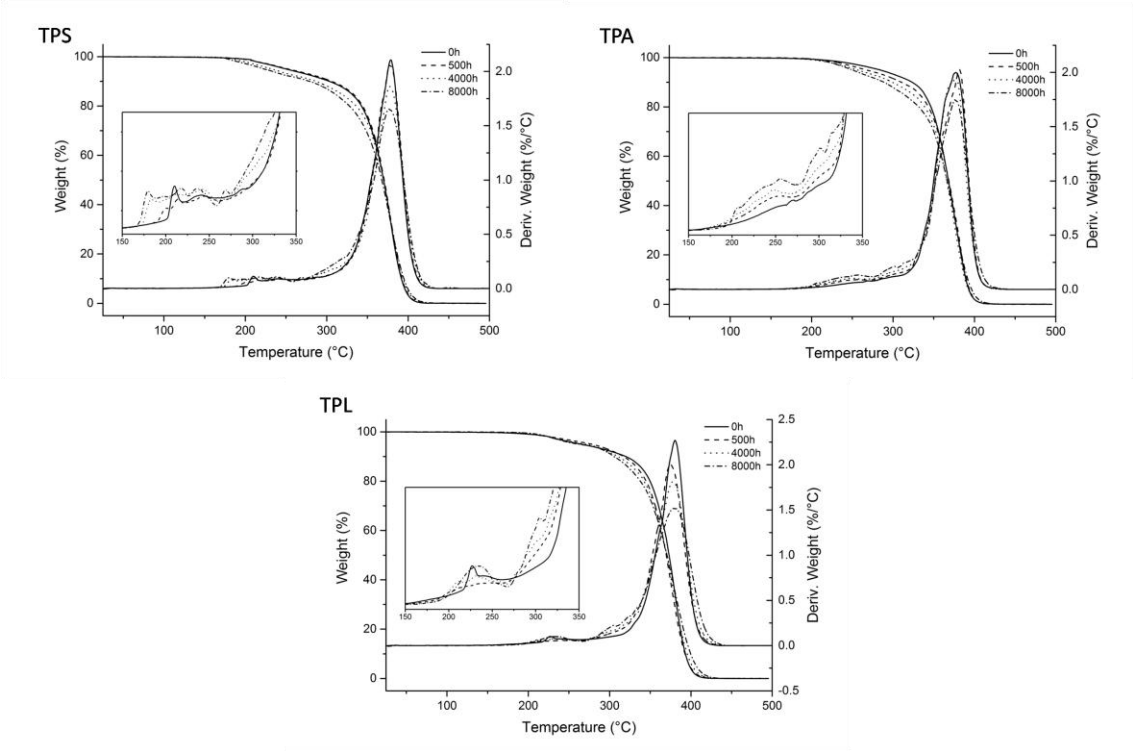


Figure 5.12: TG and DTG curves of the transparent samples after 0, 500, 2000, and 8000 h of irradiation.

5.4 Conclusions

In this work we have studied the impact of specific intrinsic factors, as additives and industrial production processes, on the properties and susceptibility of PMMA cast sheets to photooxidtion.

The data collected showed that equivalent PMMA cast sheets produced by different companies in the same period (2000s) presented different properties such as molecular weight distribution, surface hardness, or thermal behaviour. Differences were also observed in the behaviour of the samples during artificial ageing. Namely, Plásticos do Sado samples showed a higher degree of scissions per chain, higher increase in surface hardness, thermal degradation at lower temperatures, appearance of bubble like features inside the sample, and a higher development of UV fluorescence, when compared to Paraglas samples. These differences were correlated with the presence of more plasticizer in the sample composition (Table 5.4) and more defects in the

polymeric structure due to use of recycled monomer and the lack of a post polymerization step (Table 5.1). The presence of the inorganic pigment Cd(S,Se) did not seem to influence the initial properties of the PMMA sheets but might have a protective effect during photodegradation, as seen by SEC analysis and micro-hardness measurements. To the best of the authors' knowledge, it was the first time that the influence of cadmium red pigment in PMMA photodegradation was accessed.

Regarding PMMA artist's samples produced in the 1960s, it was expected that the technologies used by the two companies would be similar, and consequently, also the quality of the materials produced. However, the behaviour of the Plexiglas sheet was closer to the Plásticos do Sado reference sheet than to the Altuglas one. This is most probably related with their similar compositions, particularly in what refers to plasticizers, as shown by TD-GC/MS analysis. Nevertheless, unknown differences between the production processes of the two artist's samples cannot be ruled out either.

Surprisingly, we did not detect major differences between references from 2000s and historical artist's samples from 1960s. Therefore, with these results, we can conclude that the global production process (which may include the polymerization conditions, the monomer origin and/or the organic additives added) plays a more important role in the properties and ageing behaviour of the PMMA cast sheets than the presence of cadmium red, or the production decade of the acrylic sheets. This confirms our original hypothesis and the concerns of Lourdes Castro in the 1960s, by consciously choosing to buy what she thought were the best brands of PMMA sheet to use in her artworks.

Relevant characterization methods for assessing intrinsic properties of PMMA to help estimating their photostability were size exclusion chromatography, micro-indentation, thermogravimetry, and thermodesorption-gas chromatography/mass spectrometry.

Further research is still necessary for deeper understanding mechanisms behind the differences observed, but the results obtained show the importance of considering that not all the PMMA cast sheets are alike. This is a significant aspect when selecting testing samples for research in conservation of PMMA, and especially when considering conservation strategies for artworks made of this material. In Museum collections, the origin of the materials is most of the times unknown, but our work has proved that historical and material research may give important clues to evaluate their stability.

This is an Accepted Manuscript of an article published by Wiley:

E.M. Angelin, S. Babo, J.L. Ferreira, and M.J. Melo
'Raman microscopy for the identification of pearlescent pigments in acrylic works of art'
Journal of Raman Spectroscopy, 2019, 50: 232-241.
https://doi.org/10.1002/jrs.5431

6 Raman microscopy for the identification of pearlescent pigments in acrylic works of art

Abstract

In this work pearlescent pigments used to create lustre in poly(methyl methacrylate) artworks by Ângelo de Sousa (1938-2011) were identified in an effort to predict their possible degradation. Raman microscopy was used, in situ, to identify plumbonacrite and bismuth oxychloride. Unequivocal characterization of plumbonacrite and bismuth oxychloride was made possible by comparison with reference materials, synthesized for this study. The vibrational pattern (infrared and Raman) of both pigments is discussed. Based on their Raman ν1 stretching mode at around 1050 cm-1, we show that it is possible to differentiate between the two basic lead carbonates that are both reported in the literature to be pearlescent: hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and plumbonacrite $Pb_5(CO_3)_3O(OH)_2$. Raman microscopy was thus, for the first time, used as fingerprint tool for the molecular identification of pearlescent pigments in plastic materials. Based on these findings, better-informed conservation strategies for the acrylic sculptures will be developed.

6.1 Introduction

Pearlescent pigments have been used since the beginning of the 20th century to imitate mother-of-pearl. Mostly synthetic, they consist of flakes or thin platelet-like particles which partially reflect and partially transmit light. The pearlescent effect results from a high refractive index, smooth surfaces, optimum platelet thickness and diameter, and in addition, to a specific alignment of the platelets in the resin (Greenstein 1973; Greenstein 1988). Pearlescent pigments confer a sense of depth due to the simultaneous reflection from many layers of platelets in a parallel orientation within the resin. The effect is referred to as *nacreous luster* or *pearl luster*, distinguished from *metallic luster* where the material's surface mostly reflects incident light (Pfaff et al. 1998; Pfaff 2009).

In museum collections pearlescent pigments may be present in paints, inks, ceramics and, especially, plastic objects (buttons, bijouterie, etc.). The identification of pearlescent pigments in plastic articles is challenging owing to the small size of the particles (between 1 and 200 µm) and the low amount of pigment dispersed in the resin matrix (between 0.5 and 2%) (Pfaff and Weitzel 2004). Given this scale, Raman microscopy can be explored as a possible analytical tool for their characterization in situ.

An important Portuguese artist, Ângelo de Sousa (1938-2011) explored the properties of PMMA, poly(methyl methacrylate), in a series of acrylic sculptures executed between 1965 and 1967. These included six artworks made with white, yellow and orange lustrous sheets (Araujo 1993; Pinto de Almeida 1992). Two later works using yellow and red acrylic sheets appear to have been made by the artist in the early 2000s for a retrospective exhibition in 2006 (Faria 2006). It was important to distinguish these sculptures from his earlier work, particularly since they presented different surface effects to those from the 1960s. Ângelo de Sousa explored the thermoplastic properties of PMMA by heating, cutting and then modelling the sheets into three dimensional forms. His sculptures have various sizes, from 18 to 65 cm in height. Those made in the 1960s are characterized by a strong pearlescent lustre while the ones thought to be more recent appear more brilliant but not with the same lustre.

The identification of dyes and pigments in plastic artefacts is a recent line of research in conservation (de Groot et al. 2015; de Groot et al. 2017) and to date no publications regarding the identification of pearlescent pigments by Raman spectroscopy have been found. Understanding the original materials used by the artist is important in the interpretation of their work over time, since some materials can be susceptible to degradation which will affect their appearance. For Ângelo de Sousa's

sculptures, the difference between the original works, and those thought to be from a later date was intriguing and an explanation was sought. Furthermore, establishing the nature of the materials used allows future research into the possible mechanisms for their degradation. Therefore, in this work the use of Raman microscopy as fingerprint tool for the in situ molecular investigation of pearlescent pigments in plastic materials was explored.

The investigation was carried on lustrous acrylic sheets found in the studio of Ângelo de Sousa (Porto, Portugal), possibly the same that were used in the actual artworks (Babo et al. 2017). These acrylic sheets, one white, one yellow, one orange were likely purchased by Ângelo de Sousa from a small company active in the 1960s, *Plásticos do Sado*, which produced pearlescent acrylic sheets for the button industry (Babo et al. 2017). Two other sheets, one yellow and one red, were also found and thought to be produced in the early 2000s. In Figure 6.1 these five sheets are displayed with possible dates and correlation with the original sculptures.

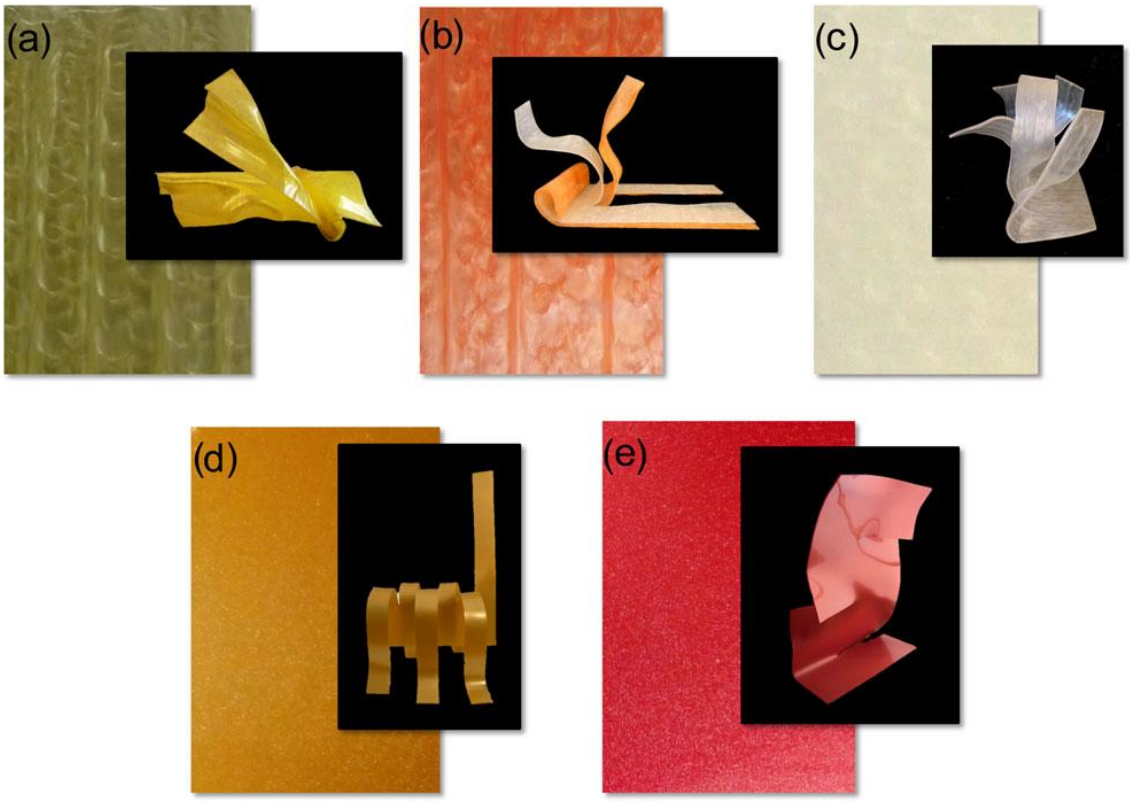


Figure 6.1: Pictures of the five pearlescent acrylic sheets found in the studio of Ângelo de Sousa (Porto, Portugal) probably made in 1960s (a-c) and 2000s (d-e). A possible match with the original acrylic sculptures by the artist is presented for each acrylic sheet

Based on a literature survey and preliminary results from X-ray fluorescence analysis, hydrocerussite (lead white), plumbonacrite and bismuth oxychloride were considered most likely to be the pigments used (Greeinsten 1988; Babo et al. 2017).

These monocrystalline pearlescent pigments were produced in the 20thcentury and used in plastics (Pfaff and Weitzel 2004; Babo et al. 2017; Webber 1979). The basic lead carbonates which are described as being pearlescent, include hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and the more basic plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ (Feller et al. 1971; Corbeil et al. 2007; Eastaugh et al. 2008). In modern manufacture the basic lead carbonate pigments both take the form of regular thin hexagonal platelets (Feller et al. 1971), making the distinction between the two different pigments by optical observation extremely difficult.

Basic lead carbonates with pearlescent properties were manufactured in the 1930s (Brossman 1937; Thompson and Alexander 1940), and by the 1950s and 1960s represented the most common synthetic pearlescent pigments employed in the production of artificial pearls, bijouterie, and acrylic and polyester buttons. From the late 1960s they started to be replaced by other pigments, such as bismuth oxychloride BiOCl due to growing concerns regarding the toxicity of lead based materials (Greeinsten 1988; Pfaff et al. 1998; Pfaff 2009; Müller 2003).

The formula $Pb_3(CO_3)_2(OH)_2$ (or $2PbCO_3{\cdot}Pb(OH)_2$) is generally reported in descriptions of the basic lead carbonates used as pearlescent pigments (Pfaff et al. 1998; Pfaff 2009; Pfaff and Weitzel 2004; Müller 2003; Ostertag and Mronga 1995). This corresponds to hydrocerussite, also known as lead white. As a mineral hydrocerrusite crystallizes in the trigonal system *R*3*m* space group (Martinetto et al. 2002) whereas synthetic plumbonacrite crystalizes in the trigonal system *P*3*c*1 space group, and is represented as pentaleadtricarbonatedihydroxide oxide, $Pb_5(CO_3)_3O(OH)_2$ (or $3PbCO_3{\cdot}Pb(OH)_2{\cdot}PbO$) (Corbeil and Sirois 2007). The currently accepted structure was proposed by Krivovichev and Burns (2000b), instead of $Pb_{10}(CO_3)_6O(OH)_6$ (or $6PbCO_3{\cdot}Pb(OH)_2{\cdot}PbO$) as proposed originally by Olby (1966). Nevertheless, $Pb_{10}(CO_3)_6O(OH)_6$ is still used in the literature, possibly due the fact that the experimental XRD pattern obtained by Olby and the calculated XRD pattern based on crystallographic data from Krivovichev and Burns are similar.

In the conservation literature, plumbonacrite was reported for the first time in the early 1970s by Feller (Feller at al. 1971) with the formula proposed by Olby (1966). Although plumbonacrite has been reported as corrosion product of lead in an acidic environment (Tétreault et al. 1998; Tétreault et al. 2003; Niklasson et al. 2008); a degradation product in stone conservation (Bersani et al. 2008); an alteration in red lead (Aze at al. 2008); and a conversion product between different lead species in lead soap

formation in paintings (Boon et al. 2002; Vanmeert et al. 2015; Cotte et al. 2016); its use as a pigment is rarely reported (Corbeil and Sirois 2007). Even though both hydrocerussite and plumbonacrite are both basic lead(II) carbonate compounds, their stability may be quite different (Taylor and Lopata 1984; Flemming et al. 1984; Haacke and Williams 1981).

Bismuth oxychloride is a rare example of a non-toxic heavy metal compound, in use since the early 1960s in cosmetics and only in the late 1960s in the plastic industry (Greeinsten 1988). It is a pearlescent pigment currently used in coatings for cars, and in cosmetics, printing, buttons, and bijouterie (Pfaff and Weitzel 2004; Suzuki 2014). As a mineral, bismoclite crystallizes in the tetragonal system *P4/nmm* space group and is characterized by thin octagonal/square platelets. BiOCl monocrystal platelets are formed by hydrolysis of acid bismuth salt solutions in the presence of chlorine ions (eg. $BiCl_3$) in water (Greeinsten 1988; Pfaff and Weitzel 2004).

In order to confirm the nature of the pigments responsible for the pearlescent lustre in the acrylic sheets found in Ângelo de Sousa's studio, and those in his sculptures, an investigation of the pigments in the acrylic sheets was carried out in situ using Raman microscopy within a multi-analytical approach which included observation under the microscope and micro-EDXRF analysis. Reference materials were required for comparison, therefore crystals of plumbonacrite and bismuth oxychloride were synthesized for this research and their composition confirmed with XRD, FTIR and Raman analyses. An analytical grade basic lead(II) carbonate without any further purification was used as the reference for the hydrocerussite.

6.2 Experimental

6.2.1 Reference Materials

All reagents used in the synthesis of the pigments were analytical grade and Millipore water was used.

Plumbonacrite

Plumbonacrite is no longer commercially available (Franz et al. 1992). Several different methods of synthesis described in the literature were tested without success (Olby 1966; Taylor and Lopata 1984; Krivovichev and Burns 2000a). Therefore, we adapted the method reported by Krivovichev and Burns which involved heating a mixture of 0.10 g of PbO and 0.10 g of K_2CO_3 in 5 ml of H_2O, in a Teflon-lined Parr bomb. This was

heated to 230°C for 36 hours. The white powder which remained in the bottom of the Teflon-lined Parr bomb was then collected by filtration and washed several times with Millipore water before being left to dry.

Hydrocerussite
A few milligrams of basic lead(II) carbonate were used without further purification.

BiOCl
Based on equation 1 proposed by Brauer, but not on his method, crystals of BiOCl were synthetized (Schenk 1963).

$$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl \text{ (eq.1)}$$

0.5 g ($1.55x10^{-3}$ mol) of bismuth(II) chloride ($BiCl_3$) were dispersed in 100 ml of water and stirred at room temperature for 30 minutes. The precipitate was collected by filtration and washed several times with Millipore water. The powder obtained was dried under vacuum for 4 hours. Reagent grade $BiCl_3$ was used without further purification.

6.2.2 Characterization methods

Optical microscopy (OM)
Optical microscopy was used to identify the shape, size, orientation and distribution of the pearlescent pigments in the plastic sheets from Angelo's studio. OM was also used to characterize the physical and optical properties of the pearlescent reference pigments. Images were acquired using a Zeiss Axioplan 2 Imageing system (HAL 100) coupled to a Nikon DXM1200F digital camera and ACT-1 software. Different illumination modes (brightfield, darkfield) were used.

Infrared spectroscopy (FTIR)
Infrared analysis was performed with a Nexus spectrophotometer in transmission mode, from 4000 to 400 cm^{-1}, with KBr pellets, 128 co-added scans and 4 cm^{-1} spectral resolution. Omnic E.S.P.5.2 software was used to perform the spectral analysis of the products. All spectra are presented as acquired without any baseline correction or other treatment.

Raman microscopy (μ-Raman)
Raman microscopy was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne 17 mW laser and a 100 mW diodes laser operating at 632.8 nm

and 785 nm respectively. Spectra were recorded as an extended scan. The system was calibrated using a silicon standard. The laser beam was focused either with a 50x or a 100x Olympus objective lens. The laser power at the surface of the samples was controlled with neutral density filters (optical densities 0.3, 0.6). Raman data analysis was performed using LabSpec 5 software. All spectra are presented as acquired without any baseline correction or other treatment.

X-Ray diffraction (XRD)

X-ray powder diffractograms were acquired with a Benchtop X-Ray Diffractometer RIGAKU MiniFlex II, using CuK_{α} radiation with a current intensity of 15 mA and a 30 kV voltage in the 2Θ range between 2° and 60° (step size of 0.01°). The ICDD PDF-2 reference database (2007) was used to interpret the XRD patterns. The Powder Cell software package was used to simulate diffractograms to compare with the experimental data (Nozle and Kraus 2000).

Micro-energy dispersive X-ray fluorescence (μ-EDXRF)

Micro-EDXRF results were obtained using an ArtTAX spectrometer (Intax GmbH) equipped with a molybdenum (Mo) anode and Xflash detector. The experimental parameters used were: 25 kV voltage and 300 μA of intensity for 360s acquisition time, under a Helium gas flux. The experimental parameters used permitted the reduction of the *bremsstrahlung* effect ("braking radiation") due to the polymeric (organic) matrix.

6.3 Results and Discussion

6.3.1 Characterization of the synthesized pigments

The synthesized plumbonacrite was observed in OM and consisted of hexagonal crystals with various diameters and thickness (Fig.A4.1, Appendix IV). The lamellar aggregation of the hexagonal crystals was also visible in OM and iridescent surface colours were observed. In the case of BiOCl, no crystals were seen with OM due to their very small dimension (<1 μm).

The composition of the crystals synthesised in this study was confirmed through XRD analysis (Fig.A4.2 and Fig A4.3 in Appendix IV). The XRD patterns of both pigments match simulations from published crystallographic data (Krivovichec and Burns 2000b; Keramidas et al. 1993) and database information for plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ (ICDD PDF 73-8925) and bismoclite BiOCl (ICDD PDF 06-0249)

respectively. Differences of relative intensities between their diffractograms and X-ray diffraction simulations are associated with the preferred orientation of the crystals.

The XRD pattern of the plumbonacrite we synthesized also corresponds to $Pb_{10}(CO_3)_6(OH)_6$ as prepared by Olby (Olby 1966) (ICDD PDF 19-0680). Therefore we assume that the plumbonacrite reported by Olby is the same basic lead carbonate that was studied by Krivovichev and Burns, although described by different formulas by the two authors (Krivovichev and Burns 2000b; Olby 1966).

The infrared and Raman spectra of plumbonacrite are shown in Figure 6.2 and Figure 6.3, together with the spectra of hydrocerussite for comparison. Raman shift values and infrared wavenumbers for the spectral features with their respective assignments are listed in Table 6.1.

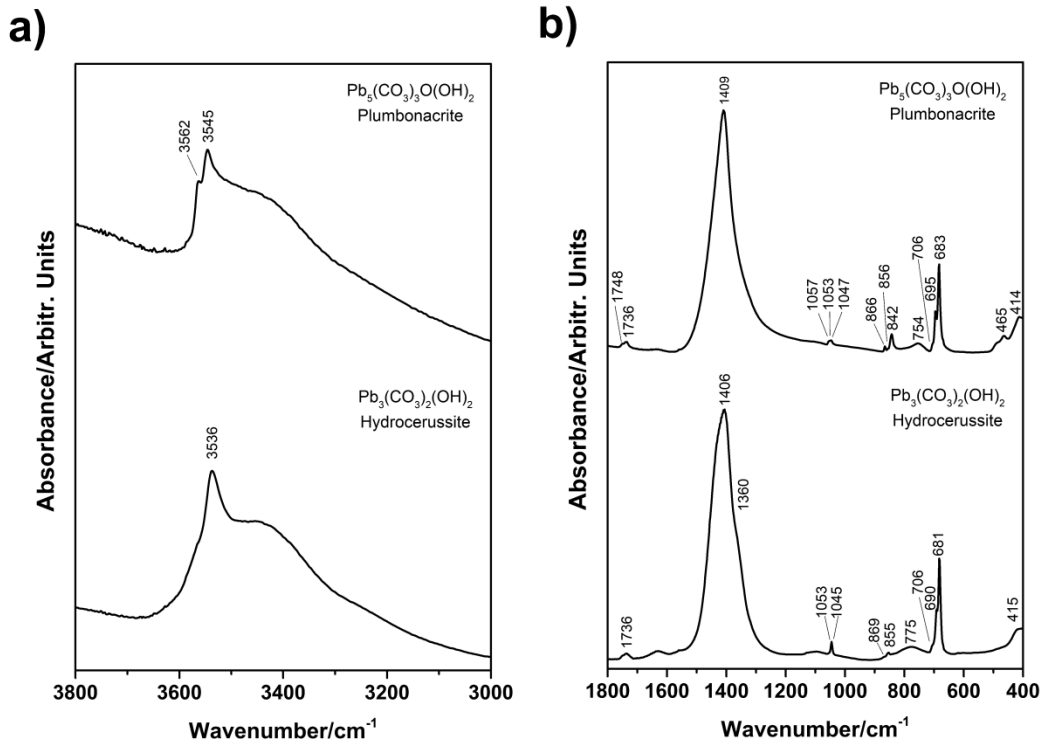


Figure 6.2: FTIR of plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ and hydrocerussite $Pb_3(CO_3)_2(OH)_2$

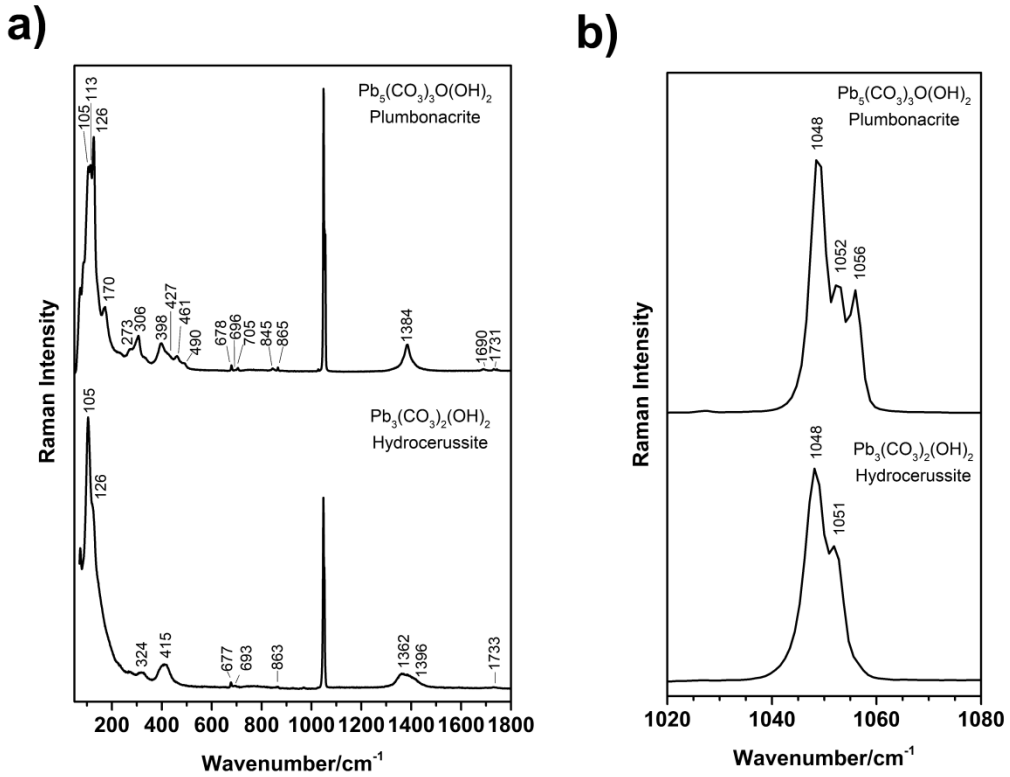


Figure 6.3: (a) Raman spectra of plumbonacrite Pb5(CO3)3O(OH)2 and hydrocerussite Pb3(CO3)2(OH)2. (b) Detail of the ν_1 stretching mode of the carbonate ion from 1020 to 1080 cm-1 (632.8 nm excitation)

In the Raman spectra, it is possible to distinguish plumbonacrite by its ν_1 stretching mode, characterized by three strong different sub-bands (1048, 1052, 1056 cm^{-1}) while hydrocerussite has only two sub-bands (1048, 1051 cm^{-1}) (Bersani et al. 2008; Brooker et al 1983; Bouchard and Smith 2003); this reflects the three and two independent sites for the carbonate ion in plumbonacrite and hydrocerussite, respectively. In the infrared spectra the two carbonates are distinguished by low intensity, but well resolved in-plane and out-of-plane bending absorptions of CO_3^{2-} between 680-710 cm^{-1} and 840-870 cm^{-1} respectively. OH stretching frequencies at 3545, 3562 cm^{-1} and at 3536 cm^{-1} in plumbonacrite and hydrocerussite, respectively, support this observation (Chukanov and Chervonnyi 2016) (Table 6.1).

The assignments for the normal modes of vibration of carbonate ion are well established, and all fundamental internal vibrations of the carbonate ion are detected between 1800 and 600 cm^{-1} (Nakamoto 2009; Herzberg 1962; Nyquist et al. 1997). Both spectra are dominated by the strong stretching associated with the carbonate ion: while a strong band associated to ν_3 mode is observed in the infrared spectra (1406 and 1409 cm^{-1} in hydrocerussite and plumbonacrite respectively) (Figure 6.2), the ν_1 mode rises to a very strong and sharp band at around 1050 cm^{-1} in the Raman spectra (Figure 6.3).

Table 6.1: Raman and infrared spectra of hydrocerussite $Pb_3(CO_3)_2(OH)_2$ and plumbonacrite $Pb_5(CO_3)_3O(OH)_2$.

Hydrocerussite		Plumbonacrite		Assignments
Raman ($\Delta\nu/cm^{-1}$)	Infrared (ν/cm^{-1})	Raman ($\Delta\nu/cm^{-1}$)	Infrared (ν/cm^{-1})	
73 m		73 m		Lattice modes
		86sh		
105 s		105 s		
		113 s		
126sh		126 s		
		170 m		
		273 m, br		
324 w,br		306 m		
		398 m		
415 m	415	427sh	414 m	ν_{PbO}
		461 m	465 mw	
		490 w		
677 w	681 s	678 w	683 s	
693vw	690 m	691vw	695 m	ν_4 (in-plane δ CO_3^{2-})
	706 sh	705 w	706 w	
	775 br		754 w, br	δ_{PbOH}
		845 w	842 w	
	855 w		856 vw	ν_2 (out-of-plane δ CO_3^{2-})
863vw	869 vw	865 w	866 w	
	1045 m			
1048 vvs		1048 vvs	1047 vw	ν_1 ($\nu_s CO_3^{2-}$)
1051 vs	1053 vw	1052 vs	1053 vw	
		1056 s	1057 sh	
1362 m, br	1360 sh			ν_3 ($\nu_{as} CO_3^{2-}$)
1396sh	1406 vs	1384 m	1409 vs	
		1690vw		$2\nu_2$
1733vw		1731vw		
	1736 w		1736 w	$\nu_1 + \nu_4$
			1748 vw	
	3536 w		3545 w	ν_{OH}
			3562 w	

m, medium; *s*, strong; *w*, weak; *v*, very; *sh*, shoulder; *br*, broad; ν, stretching (a, symmetric; as, asymmetric); δ, bending

The vibrational spectra of bismuth oxychloride is due to its isostructure (D^7_{4h} space group) characterized by two molecular formulas per unit cell with A_{1g}, B_{1g}, E_g Raman active modes and E_u, A_{2u} infrared-active modes. In the Raman spectra of

synthetized BiOCl, which is reported in Figure 6.4, both halogen sensitive and halogen insensitive bands are observed while only the A_{2u} vibration mode is detected at 528 cm^{-1} (Davies 1973; Rumolt 1972). The vibration bands with related assignments are listed in Table 6.2.

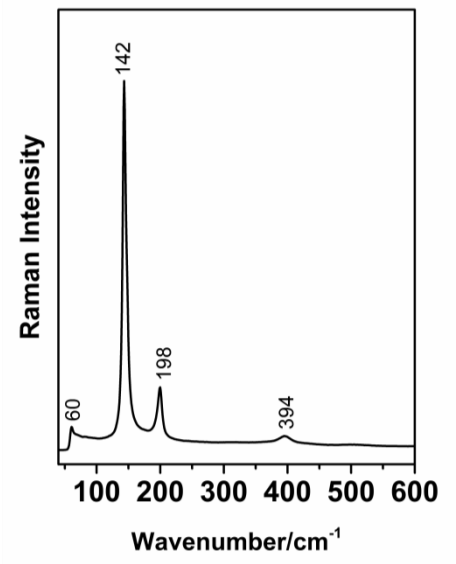


Figure 6.4: Raman spectrum of synthetized bismuth oxychloride BiOCl (632.8 nm excitation).

Table 6.2: Raman and infrared spectra of BiOCl.

BiOCl		
Raman ($\Delta\nu/cm^{-1}$)	Infrared (ν/cm^{-1})	Assignments
60 m		A_{1g}
142 vs		A_{1g}
198 s		E_g
394 m		$B_{1g} + E_g$
	528	A_{2u}

For bismuth oxychloride six Raman bands would be expected ($2A_{1g}+B_{1g}+3E_g$) however only three resolved Raman bands were found for the synthetized BiOCl. The Raman bands below 200 cm^{-1} are halogen sensitive including the A_{1g} external Bi-Cl mode (60 cm^{-1}), E_g internal Bi-Cl stretching mode (198 cm^{-1}) and the strongest A_{1g} internal Bi-Cl stretching mode (142 cm^{-1}). At around 400 cm^{-1} the E_g and B_{1g} halogen insensitive bands are not resolved resulting in a broad Raman band (394 cm^{-1}). The remnant E_g external Bi-Cl stretching mode is likely masked by the strongest peak at 142 cm^{-1}. The Raman shifts observed in the present work are similar to the reported values (Davies 1973; Rulmont 1974; Tripathi et al. 2015; Ascencio-Aguirre at al. 2017). No other peaks were observed at higher Raman shifts.

6.3.2 In situ characterization of the pearlescent pigments

By means of Raman microscopy analysis the identification of the polymer as poly(methylmethacrylate) (PMMA) was confirmed in all plastic sheets. The Raman spectrum of the polymer is presented in Fig.A4.4, Appendix IV, and the most important

absorption frequencies are listed in Table 6.3. Assignments of vibration bands were based on the literature (Ren et al. 2000).

Table 6.3: Raman wavenumbers (cm^{-1}) and assignments of PMMA.

Raman shift (cm^{-1})	Mode	Assignments
1725	ν(C=O)	stretching vibration of the C=O
1485	$\delta_{as}(CH_3)$	asymmetric bending vibration of the CH_3
1450	$d(CH_2)$	deformation of the CH_2
1389	$\delta_s(CH_3)$	symmetric bending vibration of the CH_3
1241	ν(C-C)	degenerate stretching of CC_4
1183	ν(C-C)	degenerate stretching of CC_4
1159	ν(C-O) + $\rho(CH_3)$	stretching vibration of C-O coupled with rocking vibration of the CH_3
1121	ν(C-O) + $\rho(CH_3)$	stretching vibration of C-O coupled with rocking vibration of the CH_3
1063	$\omega(CH_2)$	wagging vibration of the CH_2
986	ν(C-C)	stretching vibration C-C of the main chain
967	ν(C-C)	stretching vibration C-C of the main chain
837	d(C=O) + $\rho(CH_3)$	deformation of C=O coupled with rocking vibration of the CH_3
811	ν_s(C-C)	symmetric stretching vibration of CC_4
732	d(O-C=O) + $\rho(CH_3)$	deformationO-C=O coupled with rocking vibration of the CH_3
600	δ(O-C=O)	in-plane bending O-C=O in hydrogenbonding
552	δ(O-C=O)	in-plane bending O-C=O in hydrogenbonding
482	d(C-C)	skeletaldeformation of CC_4
362	d(C-C)	skeletaldeformation of CC_4
300	d(C-C)	skeletal deformation of CC_4

ν, stretching (a, symmetric; as, asymmetric); ρ, rocking; , δ bending(a, symmetric; as, asymmetric); τ, twisting; ω, wagging; d, deformation

Regular thin hexagonal platelet-like particles (ca. 10 µm of diameter and <1 µm of thickness) were observed with OM in the yellow and orange PMMA sheets which corresponded to the 1960s artworks (Figure 6.5 a,b). In the case of the nacreous white sample, only a few hexagonal platelets were observed (ca. 5 µm of diameter) (Figure 6.5 c), and these appeared to be very small and not well formed. Regular thin octagonal and square platelets were seen in the acrylic samples considered to be more recent (Figure 5 d,e). These were larger (ca. 15µm of diameter), and while individual platelets were well formed, there were more broken fractions dispersed throughout the acrylic matrix.

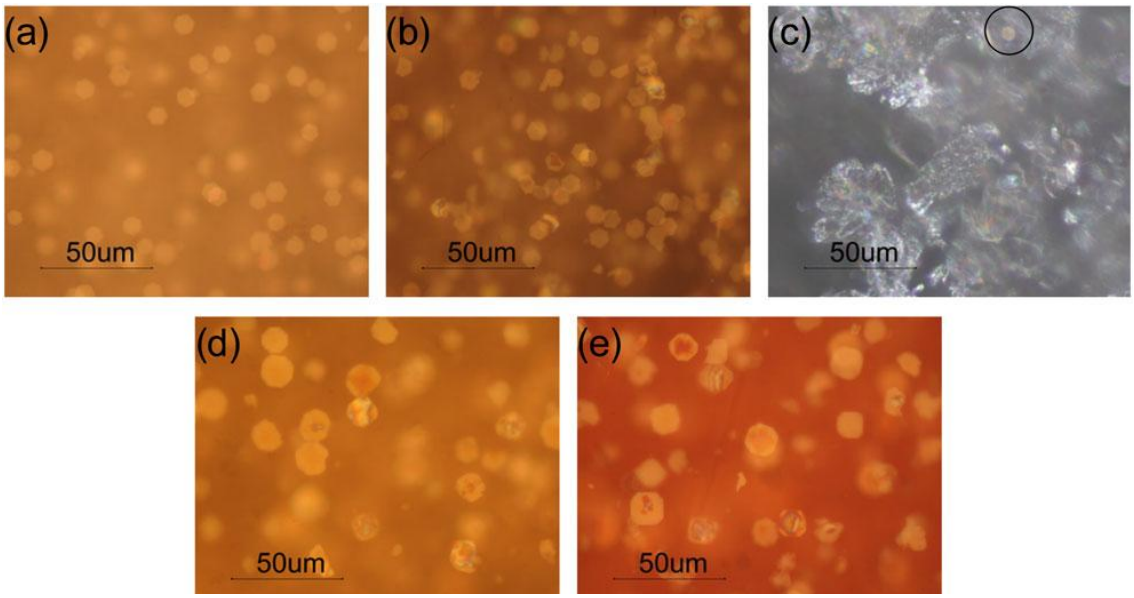


Figure 6.5: Microscopy images of the platelets in (a,d) yellow, (b) orange, (c) white and (e) red pearlescent acrylic sheet probably made in 1960s (a-c) and 2000s (d-e). A small hexagonal platelet - like particle is underlined in the pearlescent white sample (c)

The majority of the platelets in all of the plastic sheets were oriented parallel to each other and to the surface of the acrylic sheets thus producing the lustrous effect. Consequently, in cross-section only the thin sections of the platelets could be observed, while the hexagonal and octagonal/square shapes of the particle faces were only visible from the surface of the sheets. Platelets were distributed differently in the sheets dating from the 1960s versus those thought to be from the early 2000s. A greater sense of depth in the 1960s sheets was achieved by the highly irregular dispersion of pigment platelets (Fig.A4.5 a,b in Appendix IV). As reported by Babo et al. (2017) this final appearance had been designed intentionally by the Portuguese company *Plásticos do Sado*. In contrast the completely homogeneous appearance of the more recent sheets was achieved by a uniform distribution of the platelets (Appendice IV, Figure A4.5 c,d).

Focusing the Raman laser beam on the hexagonal platelets in the acrylic sheets, a peak centered at around 1050 cm^{-1} was observed (Figure 6.6a). This peak, not assignable to the vibrational fingerprint of PMMA, suggests the presence of the crystal phase of plumbonacrite due to the factor-group splitting of the ν_1 symmetric stretching mode of the CO_3^{2-} ion. A division in three different sub-bands (1048, 1052 and 1056 cm^{-1}) is also observed in the Raman spectrum of the synthesized plumbonacrite (Figure 6.6b) supporting its identification in situ in the acrylic sheets.

Bismuth oxychloride was identified in the more recent acrylics by the detection of three bands (142, 198 and 394 cm^{-1}) in the region between 100 and 400 cm^{-1} (Figure

6.7a) which matches the position and relative intensity of the Raman bands for synthesized bismoclite BiOCl (Figure 6.7b). To perform Raman microscopy analysis on the yellow acrylic sheet, the 785 nm excitation wavelength was used to avoid florescence which occurred at 628.3 nm likely due to the dye present as colorant in the acrylic sheet.

The identification of plumbonacrite and bismuth oxychloride is also supported by µ-EDXRF results. Lead (Pb) was detected in the hexagonal platelets while bismuth (Bi) and chlorine (Cl) were detected and associated in the octagonal/square platelets.

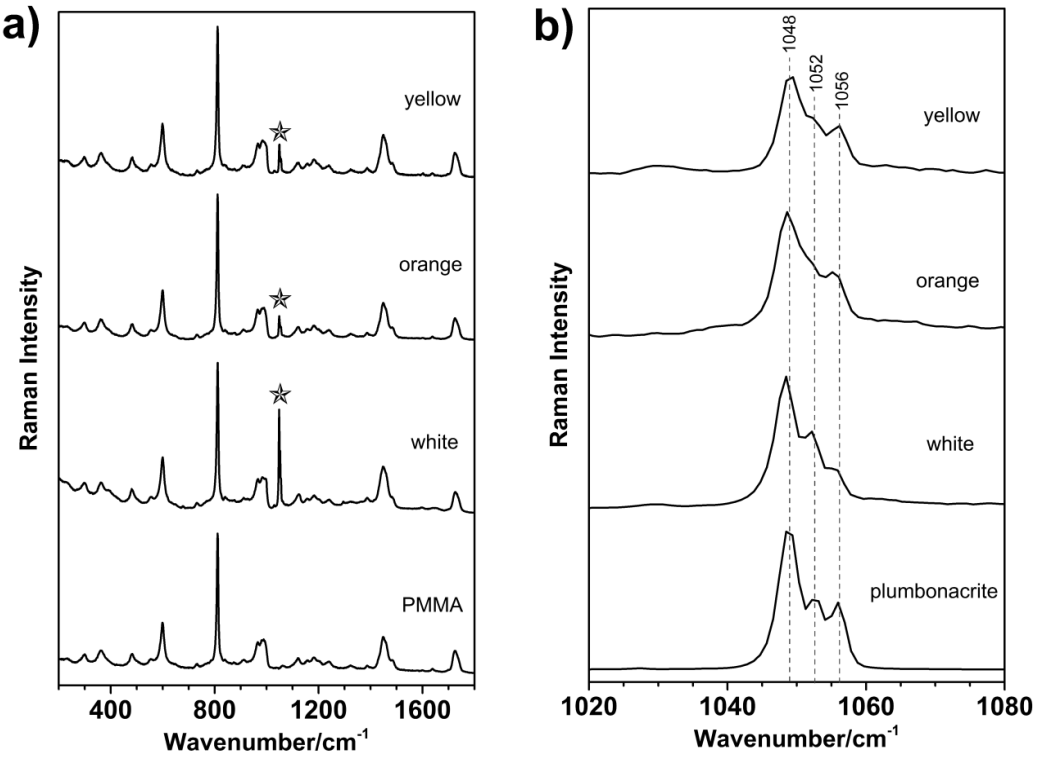


Figure 6.6: Raman spectra of the hexagonal platelets in yellow, orange, and white pearlescent acrylic sheets dated from 1960s. The Raman spectra of PMMA and synthesized plumbonacrite are also reported for comparison. Peaks centered at around 1050 cm^{-1} are marked with a star in (a) and seen in detail in (b). These bands are associated to ν_1 symmetric stretching mode of the CO_3^{2-} ion (632.8 nm excitation).

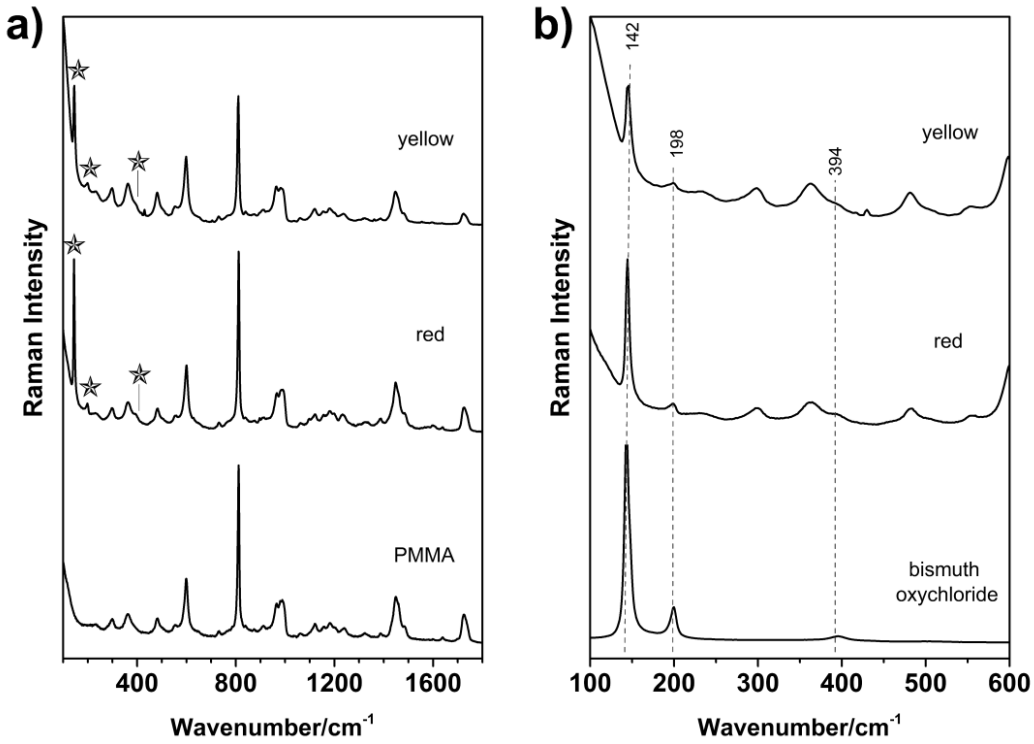


Figure 6.7: Raman spectra of the square/octagonal platelets in yellow and red pearlescent acrylic sheets dated from the 2000s. The Raman spectra of the square/octagonal platelets in the red and yellow sheets are acquired in situ with 632.8 and 785 nm excitation, respectively. The Raman spectra of PMMA and synthetized bismuth oxychloride are also reported for comparison. Peak at 142, 198, and 394 cm^{-1} are underlined.

6.4 Conclusions

Raman microscopy proved to be a valuable technique for the identification of pearlescent pigments in plastic materials. For the first time, plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ and bismuth oxychloride BiOCl were identified in situ using Raman microscopy. Despite the low amount of pearlescent pigment dispersed in the acrylic polymeric matrix (max 2%), it was possible to obtain molecular information at the micrometer-scale by focusing the laser beam on the platelets' surfaces, taking advantage of the confocal system associated with the Raman equipment. The vibrational fingerprint of the pigments was obtained by observing some Raman bands not assignable to the PMMA Raman spectrum. These were identified using synthesized pigments to provide the reference bands. The identification of the two different pearlescent pigments supports the dating of the acrylic sheets and the artworks. In fact, the pigment identification agrees with the literature, since as previously stated, from the second half of the 20th century, basic lead carbonates were progressively replaced by

BiOCl due to the toxicity problems associated with lead compounds (Greeinsten 1988; Pfaff at al. 1998).

This work clarifies that the basic lead carbonate used in the 1960s acrylic sheets studied was plumbonacrite $Pb_5(CO_3)_3O(OH)_2$, rather than hydrocerussite $Pb_3(CO_3)_2(OH)_2$. This identification evidences the use of plumbonacrite as pearlescent pigment by the plastic industry, which was never specifically reported in the colouring technology literature. In fact, pearlescent lead pigments are simply referred as basic lead carbonate defined by the formula for hydrocerrusite. The presence of plumbonacrite in the sheets dated from 1960s and bismuth oxychloride in those thought to date from 2000s also explains the difference in their appearance. While plumbonacrite is recognized to be a nacreous pigment, bismuth oxychloride is considered to be more metallic and brilliant in appearance (due to its higher refractive index, n=2.15) (Greeinsten 1988). The differences between the two in terms of pigment distribution in the acrylic matrix also accounts for the different visual effects.

Raman microscopy to identify the two pigments in situ will lead to better informed strategies for the preservation of Ângelo's plastic sculptures. The limited chemical stability of basic lead carbonates (Pfaff at al. 2012) and the low light stability of BiOCl to UV radiation (Greeinsten 1988; Pfaff and Weitzel 2004), will inform the design of new guidelines for their storage and exhibition.

This is an Accepted Manuscript for publication by Die Neue Sammlung – The Design Museum:

S. Babo, J. L. Ferreira, A. M. Ramos, M. J. Melo.
‘Surface treatment of acrylic sheet: evaluating cleaning and polishing commercial products used by Lourdes Castro’.
Future Talks 019 – Surfaces. Lectures and workshops on the conservation of the Modern. Ed. T. Bechthold (in press).

7 Surface treatment of acrylic sheet: evaluating cleaning and polishing commercial products used by Lourdes Castro.

Abstract

This work investigates the immediate and long-term effect of commercial products for cleaning and polishing acrylic sheet (PMMA), as used by one of the most important Portuguese artists working with this material, Lourdes Castro (b. 1930). Since these products (Altuglas® Cleaner and Polishers) have been commercialized by one of the main producers of acrylic sheet, it can be assumed that they have been used by other artists or art collectors. However, these ready-to-use products have possibly been developed without the same concerns conservators have. Therefore, their performance was tested and compared with the use of distilled water + non-ionic detergent, as generally recommended for plastic artefacts in museum collections. Different types of PMMA sheets were used as testing samples; the effect of repeated cleaning and polishing actions during the lifetime of an artwork was reproduced by submitting the samples to several cycles of cleaning and/or polishing followed by artificial ageing in a solarbox. Samples were periodically characterized by optical microscopy, colorimetry, gravimetry, micro-indentation, infrared and Raman spectroscopies, and size exclusion chromatography.

7.1 Introduction

Lourdes Castro is one of the major figures of Portuguese art. She was born in the Portuguese island Madeira in 1930, moved to Lisbon in 1950 to study fine arts, and in 1958 to Paris, where she worked for 25 years. In 1983 she returned to Madeira. Lourdes Castro has devoted most of her career to the subject of Shadow. She collected the projected shadows of her friends and family, but also of everyday objects and plants (Pereira 1992; Fernandes and Zimbro 2003). For her, this was a way of contemplating things and people around her (Castro 2010). She has explored this theme in different supports, from oil painting to theatre, but acrylic sheet was especially relevant during the 1960s. In 1966 the artist stated that 'Searching for a material without texture and more in agreement with the result I wanted, I made, in 64, my first essay in plexiglas. At last, an immaterial material like the shadows.' (Pereira 1992). This "immaterial" aspect comes from the impeccable transparency of acrylic sheet, or more accurately poly(methyl methacrylate), PMMA, sometimes also referred to as organic glass.

Because PMMA is soluble in its own monomer, it can be synthesized in bulk by chain (radical) polymerization slowly and with very few impurities, resulting in a polymer with outstanding optical properties (Painter and Coleman 2009), which was a fundamental aspect in its development as a substitute of glass. Research into acrylics started in the 2nd half of the 19thcentury but it was only in the early 1930s that acrylic sheet from PMMA began to be produced at an industrial scale. Depending on the company that produced them, these sheets were commercialised under different trade-names, such as Plexiglas® (Rohm and Haas, DE and USA), Perspex® (ICI, UK), Lucite® (DuPont, USA) or Altuglas® (Altulor, FR). In Portugal the two main producers of acrylic sheet were Paraglas (connected to the German Degussa) and Plásticos do Sado (a family business), (Babo et al. 2017).

PMMA is recognized for its outstanding resistance to weathering, being especially stable to photo-oxidation, which has been well studied (Fox et al. 1967; Rabek et al. 1995; Melo et al. 1999; Chiantore et al. 2000). Its stability is partially explained by the fact that the polymer does not absorb radiation above 320nm (i.e. light filtered through a glass window) and absorbs mainly under 285nm (radiation that hardly reaches the Earth surface). Nevertheless, light absorption occurs by impurities that are present as consequence of synthesis and processing. These, however, do not have a catalytic influence on the polymer degradation, since the photo-oxidative degradation results in chain splitting with no side reactions leading to the build-up of chromophore species (Davis and Sims 1983; Ferreira et al. 2011). Therefore, PMMA objects are more resistant to light than most of the objects made from other plastics.

Even so, PMMA artworks pose considerable challenges regarding their conservation, mainly in what concerns their surface tendency to attract dust, their high susceptibility to abrasion and scratches (Shashoua et al 2009; de Sá et al. 2011), and the risk of having internal stress due to manufacturing and processing techniques or solvent exposure, which may lead to crazing (Sale 1993; Waentig 2007; Shashoua 2008). Therefore, simple actions such as cleaning may be problematic, which justifies why research has been conducted to find effective and safe procedures during the last decade (Casella and Moore 2009; Shashoua et al. 2009; Balcar et al. 2012; Kavda et al. 2017). Regarding the treatment of abrasion and scratches, polishing is a common solution but since it implies removal of original material it raises ethical questions; for this reason, alternative methods such as filling the scratches have been explored (Kim and Breitung 2007; Laganà et al. 2017). Damages in acrylic surfaces are especially disturbing in face-mounted photographs, which might explain why pioneer studies on the treatment of acrylic surfaces arose initially from the conservation of photography field (Penichon and Jurgens 2001; Murphy 2007; Wey 2008).

In the previously mentioned works, research was focused in finding the best methods to clean or remove scratches from acrylic surfaces. In the present work, a different goal has been followed: we focused on evaluating the impact of the commercial cleaning and polishing products from Altuglas, as used by Lourdes Castro, on the photodegradation of PMMA.

For finishing the edges of her artworks, Lourdes Castro used a kit of commercial polishing products specifically sold to be applied in Altuglas acrylic sheets. Accordingly to a letter by the artist (Ferreira 2011) she would use first Altupol 1, followed by Altupol 2, which were applied with a cotton pad or cotton cloth. Light surface scratches were also removed with these polishing products. As a final treatment, and also as a maintenance procedure, the artist would wash the acrylic shadows with water and soap, and after drying with a smooth cotton cloth, she would apply Altunet as an antistatic agent with a special smooth cloth.

Altupol and Altunet were products from Altulor, the name of the French company that produced Altuglas (PMMA sheet). Altulor was created in 1957 from the union of Alsthom and Ugilor and during its history it was part of several merges and separations of big companies and petrochemical groups, including the union of Elf Atochem and Röhm und Haas in 1992, which ended up with the name Altulor and turned into AtoHaas. Even so, the commercial name of the PMMA sheets produced remained Altuglas® and, in 2004, the name of the company with production and commercialization rights became Altuglas International, subsidiary of Arkema group.

(Michel 2012; Arkema n.d.). Accordingly, Altupol polishers became Altuglas Polish 1 and Polish 2, and Altunet became Altuglas Cleaner.

As these products have been commercialized by one of the main producers of acrylic sheet, it can be assumed that they have probably been used by other artists and art collectors. However, these ready-to-use products have possibly been developed without the same concerns conservators have, and therefore need to be tested in relation to their long-term impact on artworks. To this end and continuing the research begun by Ferreira (Ferreira et al. 2011), this work is aimed at responding to the following questions:

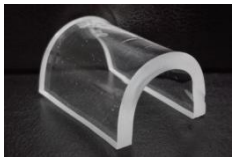
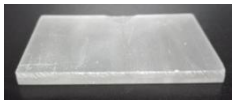
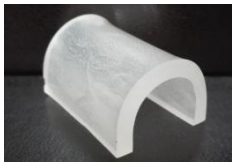
- Are these products/methods safe in the long-term?
- Is the effect of this products/methods independent of the type of PMMA in which are applied (e.g. new vs old; transparent vs. opaque/coloured)?
- Is their effect independent on the type of transformation the PMMA has been subjected (e.g. being thermoformed or not)?

7.2 Methodology

To access the possible long-term impact of the Altuglas products in different types of PMMA artworks, testing samples aimed to cover different typologies, namely: 1) transparent vs. non-transparent sheets; 2) recent vs old material; 3) plane vs. thermoformed sheets. In this way, samples of 3x5cm were cut from two types of cast PMMA sheets: a transparent sheet, from 2007, produced by Paraglas; and a nacreous translucent sheet, from the 1960s, most probably produced by Plásticos do Sado[15] using the special effect pigment synthetic plumbonacrite to produce the nacreous effect (Angelin 2019). These two typologies of acrylic sheet were characterized in our previous research (Babo et al. 2017, 2020), and have shown different properties and long-term stabilities which were related with production details and composition. In order to test also the influence of thermoforming, half of the samples were heated above their glass transition temperature (Tg) and bended in a U shape. The PMMA typologies of samples under testing are presented in Table 7.1.

[15] The nacreous acrylic sheet under study was found in the studio of Ângelo de Sousa, a Portuguese artist who also explored PMMA during the 1960s in his artworks. He used the PMMA available in Portugal, which was produced by Plásticos do Sado (Babo et al, 2017).

Table 7.1: Typologies of PMMA samples under testing.

Code	Image	Description	Brand	Date	Colorants identified (Raman)
TPA—		Transparent Plane	Paraglas	2007	–
TPA U		Transparent Thermoformed			
NW—		Nacreous white Plane	Plásticos do Sado*	1960s	Synthetic plumbonacrite, $Pb_5(CO_3)_3O(OH)_2$
NW U		Nacreous white Thermoformed			

* Sheets bought in the 1960s by the Portuguese artist Ângelo de Sousa.

Samples were cleaned with the Altuglas products and water with non-ionic detergent for comparison[16], as described in Table 7.2. A total of 16 testing samples were tested, consisting of four treatment methods and four PMMA typologies. The cleaning agents were applied with a soft cotton cloth which was immersed in the cleaning agent and excess of liquid was squeezed. Surfaces were cleaned in five unidirectional movements with a moderate pressure for approximatly 10 s. For the Polishers, product instructions were respected and treatment was performed with circular movements during the amount of time necessary for the product to disappear, approximately 30 s. We opted for not wiping or rinsing afterwards since we were also interested in determining the consequences of any residues left on the surfaces.

All samples were artificially aged by photodegradation in a solarbox, under xenon-arc lamp irradiation (800 W/m^2, $\lambda > 300$ nm), for a total amount of 4000 h. To simulate the accumulation effect of cleaning or polishing actions in an artwork during its life, every two weeks (ca. 336 h), the ageing experiment was interrupted and samples

[16] Non-ionic detergent in distilled water is the main recommended cleaning procedure for PMMA (Balcar et al, 2012).

were subjected to cleaning/polishing procedures, which meant a total of 12 cycles of cleaning/polishing followed by ageing.

Table 7.2: Types of treatments tested in each PMMA sample typology.

Code	Symbol	Description
1		Distilled water + detergent (Neutracon 1%); followed by distilled water
2		Altuglas Cleaner
3		Distilled water + detergent (Neutracon 1%); followed by Altuglas Cleaner
4		Altuglas polish 1; followed by Altuglas polish 2

A protocol of analysis was established to access the possible effects of the treatments on the PMMA samples surface. This included assessment of optical, physical and chemical changes. Optical assessment was based on visual observation with naked-eye, observation by optical microscopy (OM), and colorimetry. OM images were collected with reflected light, in dark and bright fields, with 50x, 200x and 500x total magnifications; these are fundamental to detect creation or removal of scratches. For colorimetry, L*, a*, and b* colour coordinates were determined and colour variation (ΔE^*) was calculated. Three measurements per sample were performed, using a mask to guarantee measurements were always done at the same points. Although colorimetry is useful to detect subtle colour changes, it is not indicated for transparent samples; therefore, we used a white base under the sample (composed of several layers of lab filter paper) to detect any eventual yellowing of the samples. The same base was used in all measurements and stored in the dark in between.

Assessment of physical changes was performed using gravimetry and Vickers hardness test. Regarding gravimetry, a decrease on the weight of the samples could reflect the loss of material due to abrasion during treatments, but also due to the loss of volatile degradation products during ageing; an increase would probably be associated with any residues from the tested products left on the surfaces and/or water absorption. Each sample was weighed three times at each control time. Vickers hardness test was selected as a method to detect eventual mechanical changes on the material surface, since it measures hardness on a micro-scale. Because of the high sensitivity of this technique to changes on the PMMA surfaces resulting from moisture uptake due to the

relative humidity in the room, all measurements were performed in the same day, after stabilizing the samples for two weeks in a desiccator. Five measurements per sample were performed.

Finally, assessment of chemical alterations was conducted by infrared (FTIR-ATR) and Raman spectroscopies, and size exclusion chromatography (SEC). The spectroscopic techniques were aimed at detecting eventual formation of degradation products or residues from the products left on the surfaces; and SEC to detect alterations on the molecular weight of the samples due to chain scission. SEC was the only technique that required sampling, on the order of 2±0.5 mg. Material was removed from the PMMA surfaces using a scalpel and solubilised in tetrahydrofuran (THF). For each testing sample, three samples were collected, solubilised, filtered and injected.

Analysis were performed in all samples before ageing, and after 2000 h and 4000 h of artificial ageing, except for Vickers test and SEC, which were only performed for the 4000 h aged samples. The shape of the thermoformed samples did not allow colorimetry and micro-indentation to be performed. Additional information regarding equipment and acquisition details may be requested from the authors.

7.3 Results and discussion

7.3.1 Characterization of Altuglas cleaning and polishing materials

Since the information provided by the manufacturer about the Altuglas® products under testing was very general, the first step was to characterize them further. Table 7.3 resumes the main results obtained. The datasheet of Altuglas® Cleaner describes the product as ‘an emulsion of silicone oil and cationic detergent in water’ (Altuglas International, 2006). Analysis by FTIR-ATR confirmed the presence of a silicone, most probably poly(dimethyl siloxane). Altuglas® Polish 1 is in turn described as ‘a mixture of mineral abrasives and saps in aliphatic hydrocarbons with an aromatics content of less than 5 %’ (Altuglas International, 2009a). Elemental analysis by x-ray fluorescence (XRF) detected the presence of Ti and Fe. By Raman spectroscopy, it was possible to relate the Ti element with anatase (TiO_2) which is possible one of the mineral abrasives present in the composition. Kaolin and quartz were identified by infrared spectroscopy (FTIR) and are likely to be present also as abrasives. FTIR analysis could further confirm the presence of the hydrocarbon compound. Altuglas® Polish 2 is again described as ‘a combination of mineral abrasives’ but in a ‘mixture of water and aliphatic hydrocarbons with an aromatics content of less than 5 %’ (Altuglas

International, 2009b). XRF analysis identified the presence of Al, K and S, most probably related with clay which may be the abrasive component. It was not possible to identify in depth the organic part.

Table 7.3: Characterization of the treatment products under testing

	Altuglas Polish 1[a]	**Altuglas Polish 2[b]**	**Altuglas Cleaner[c]**	**Neutracon detergent**
Datashet information	Mineral abrasives; aliphatic hydrocarbons; aromatic solvents	Mineral abrasives; aliphatic hydrocarbons; aromatic solvents; water	Silicon oil; cationic detergent; water	Anionic and non-ionic surfactants; Water; polyhydric alcohol
XRF	Ti, Fe	Al, K, S	-	-
FTIR	Kaolin; quartz; hydrocarbon compound	n.c.	Poly(dimethyl siloxane)	-
Raman	Anatase	n.c.	-	-

[a] Previously Altunet; [b] Previously Altupol 1; [c] Previously Altupol 2; n.c.= not conclusive

7.3.2 Impact of the different treatments on the PMMA samples

Optical alterations

No significant changes were detected by visual (naked-eye) observation on all testing samples after treatment; this was expected since the testing samples were not initially dirty. Also, no significant differences were detected during artificial ageing on the transparent (TPA) testing samples between the different treatments or in comparison with the control (untreated, not artificially aged). Regarding the nacreous white (NW) testing samples, a severe darkening was observed during artificial ageing. This effect was observed both in the treated testing samples and control, and is related with an alteration of the pigment responsible for the nacreous effect, the synthetic plumbonacrite (Babo et al. 2017b). Also, on the NW material, after 4000 h, bubbles were formed on the surfaces as well as severe cracking on all the testing samples except NW/4 (treated with the polishers). One explanation might be that because of the darkening of the samples, the temperature of the surfaces raised during the photodegradation, inducing also some thermal degradation; the bubbles could be due to released products trapped in the polymeric matrix. On the curved samples similar tendencies were observed. Probably due to the curved shape of the samples, more residues of the polishers remained on the surface and were visible with naked eye.

Observation by optical microscope was more informative. Both TPA and NW testing samples subjected to treatment 1 (cleaning with water and detergent) did not show relevant differences before and after cleaning besides the removal of minor deposits and the appearance of additional minor scratches. Treatment 2 (cleaning with Altuglas® Cleaner) was able to disguise part of the scratches on the original surfaces, apparently by filling them, however, additional minor scratches have also appeared. In addition, residues from the Cleaner were observed in both types of PMMA, which appear as small dots on the surfaces. Testing samples submitted to treatment 3, water cleaning followed by Altuglas® Cleaner, showed the same alterations as with treatment 2, with an increase of the Cleaner residues. Regarding treatment 4, polishing with Altuglas Polish 1 and 2, most of the scratches on the surfaces were in fact removed; however, additional scratches were created during treatment. Improvements on the surface were mainly visible on the NW samples, which were initially more damaged. As expected, residues of the products were visible on the surfaces of both types of PMMA. Figure 7.1 shows the surfaces of TPA plane testing samples before and after the different treatments for comparison.

In what concerns the alteration of the PMMA surfaces after the cycles of treatment and artificial ageing, in general, TPA testing samples remained almost unaltered during artificial ageing while on NW samples alterations were observed, namely the appearance of micro-cracks, already after 2000 h of artificial ageing. This feature was also visible on the untreated samples. Nevertheless, for the studied samples it is possible to affirm that micro-cracks have developed mainly on the nacreous samples treated with Altuglas Cleaner (treatments 2 and 3), Figure 7.2. Since this type of PMMA is very heterogeneous, other factors related with the composition of the material might be having an influence and it may be worth to further investigate this apparent tendency. The thermoformed samples do not seem to have developed as much micro-cracks as the plane ones. One possible explanation might be that the thermoforming process promotes the realignment of the polymer chains in a tighter way, with less free volume, which reduces the oxygen diffusion and consequently improves the resistance of the polymer to photo-oxidation.

Colorimetry did not reveal significant colour changes on the TPA samples after treatment and after ageing. The maximum ΔE^* value obtained was 2.16 for the TPA/1 testing sample after 4000 h of ageing, which is under the JND (just noticeable difference) limit of 2.3 [Mokrzycki and Tatol, 2012]. Results obtained for the NW samples were not considered since the severe darkening of the samples is most probably related with a photo-induced reaction on the lead pigment (Babo et al 2017b), and not with the effect of the treatments on the PMMA. Measurements on the curved

thermoformed samples were impossible to perform due to the geometry of the samples, which did not allow the full contact of the colorimeter head.

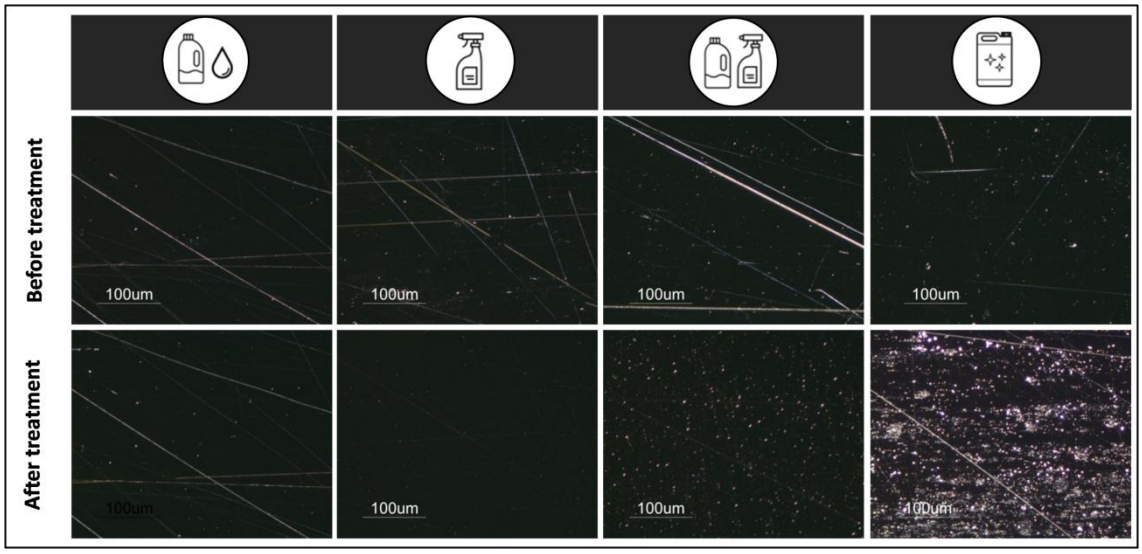


Figure 7.1: Optical microscope images (dark field) of the TPA test samples surfaces, before and after treatment with the four different methods.

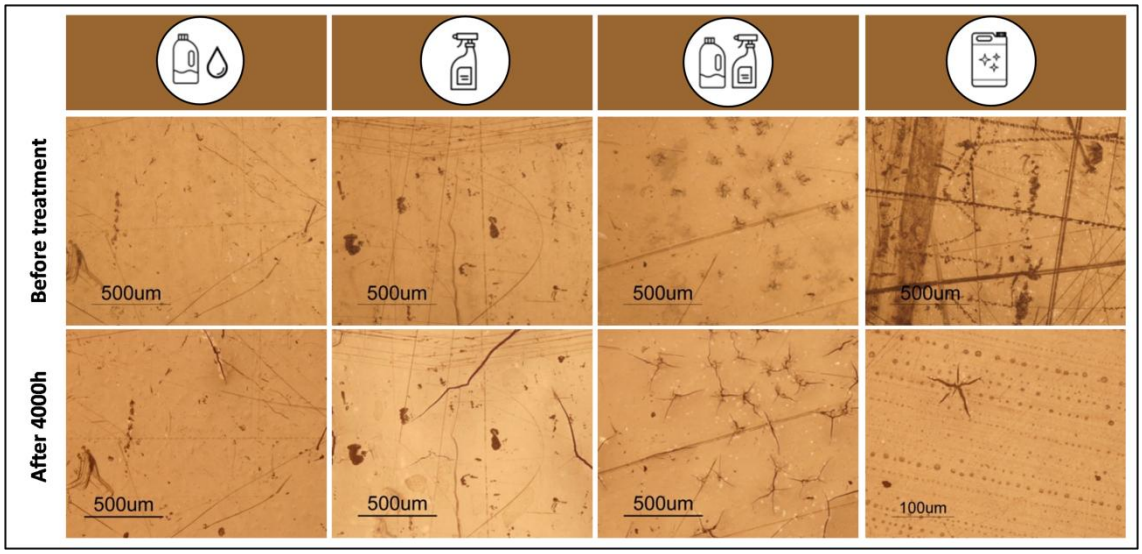


Figure 7.2: Optical microscope images (bright field) of the NW test samples surfaces, before treatment and after 4000 h of artificial ageing with treatment and photodegradation cycles.

Physical Alterations

Mass variation

Gravimetric analysis did not show significant mass changes of the samples (loss or gain). All variations, in percentage of original mass, were under 0.2 % after

treatment, being the highest values obtained for the thermoformed samples. Regarding variations during artificial ageing, values obtained were also very low, under 0.5 % after 2000 h, and between 0.2 % and 1.2 % after 4000 h. Variation was always superior on the NW samples, independently of the treatment tested. It may be concluded that the treatments under testing did not seem to have a significant effect on the mass variation of the samples.

Micro-hardness (Vickers testing)

Figure 7.3 represents the Vickers hardness obtained for a load of 0.3 kgf and 15 s loading time on the surface of the plane testing samples. Values are an average of 5 indentations per sample; the difference in homogeneity between the TPA and the NW surfaces, previously observed in the MO images, is here reflected on the error bars, which are larger for the NW samples. It was not possible to perform measurements on the thermoformed (U) testing samples due to their conformation.

The micro-hardness of TPA testing samples remained practically unaltered during ageing and independently of the treatment tested. The small differences observed are under the error associated with the measurement. In turn, an increase in hardness was observed with ageing for all the NW test samples. Given that all obtained values fall within the error bars, it is possible to conclude that this increase is independent of the type of treatment performed.

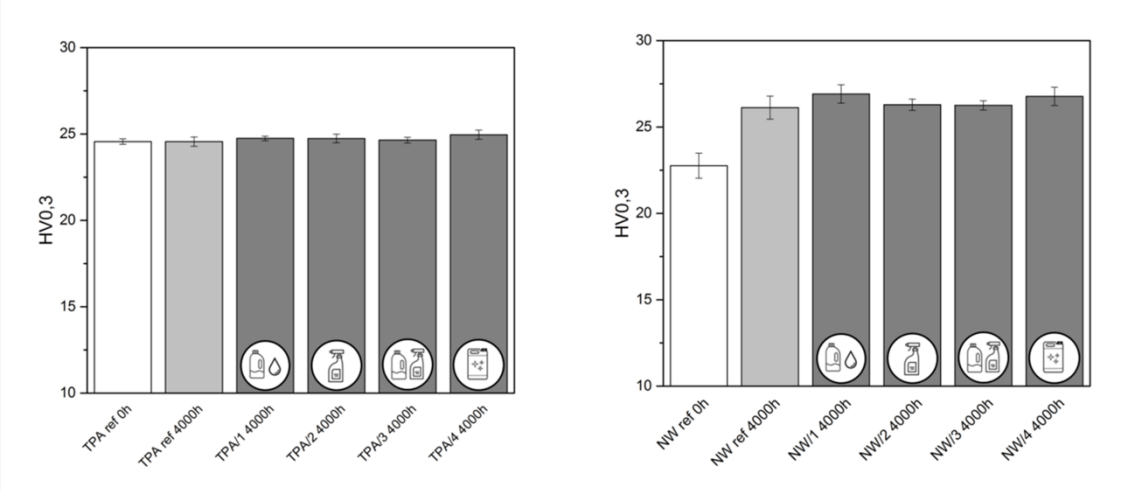


Figure 7.3: Average Vickers hardness (0.3) values obtained for TPA (left) and NW (right) test samples.

Chemical alterations

The FTIR-ATR spectra obtained for all the testing samples correspond to PMMA homopolymer and significant changes were not detected after treatment and after artificial ageing, Figure 7.4. Raman spectroscopy was also unable to detect differences between the molecular composition of the testing samples before and after treatments and artificial ageing or remnants of the treatment materials used.

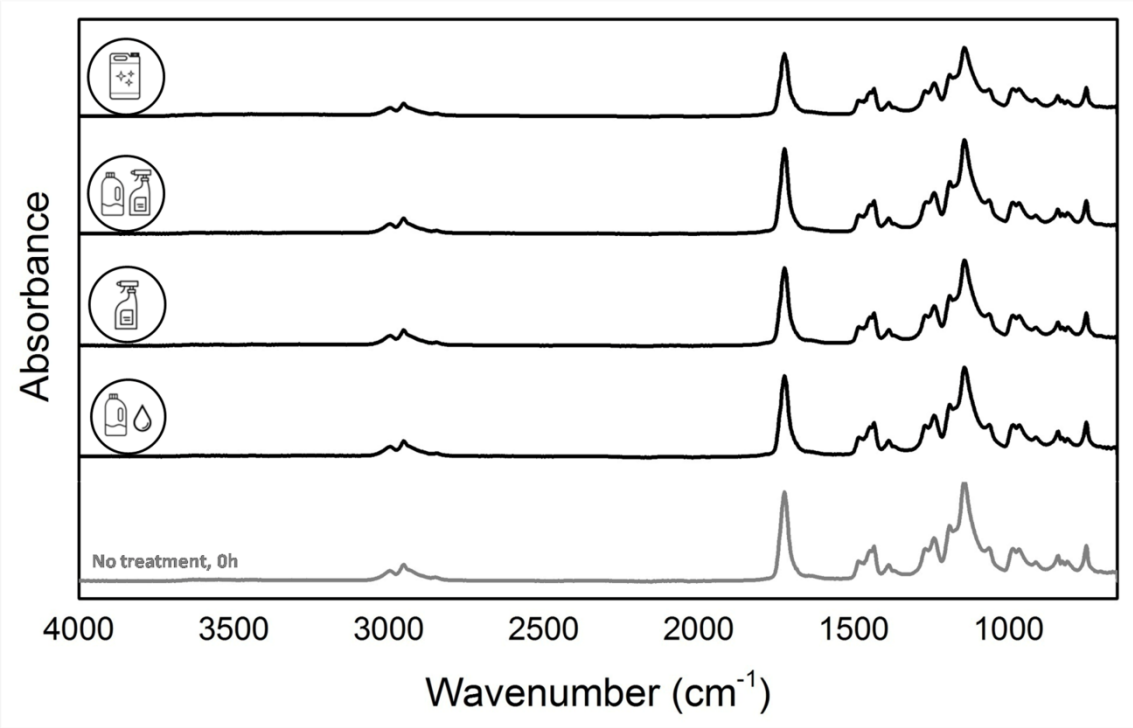


Figure 7.4: : Infrared spectra of NW curved samples. In grey, uncleaned samples before artificial ageing; in black, from bottom to top, samples with treatments 1 to 4 after 4000 h artificial ageing.

In contrast, size exclusion chromatography (SEC) proved to be a fundamental technique to follow PMMA chemical degradation. In Table 7.4 values for weight average molecular weight (M_w), and polydispersity ($Đ_M$) of each test sample are shown. In addition, the number of scissions per chain was calculated from the values of number average molecular weight (M_n) using the formula Mn_{0h}/Mn_{4000h}-1 and presented in Figure 7.5. A dramatic reduction in molecular weight, corresponding to a decrease of one order of magnitude on M_w, was observed after the 4000h of artificial ageing in all test samples, including the non-treated control samples. Since all samples remained soluble after the artificial ageing, it may be concluded that chain scission was the main degradation mechanism occurring during the experiment, which is in agreement with

the literature (Fox et al 1967; Rabek et al. 1995; Melo et al. 1999; Chiantore et al. 2000).

Significant differences between TPA and NW samples are again clearly visible, Figure 7.5. Apparently, in TPA samples the effect of the different treatments in comparison with untreated samples is negligible on the plane samples, or even beneficial in the thermoformed ones. No explanation could be found for this improvement only in the thermoformed samples and further research is necessary. On the contrary, all treatments seem to have a negative effect on the NW samples, contributing to a chain scission increment on both plane and thermoformed samples. This is possibly related with the development of micro-cracks on the surface of these samples during the artificial ageing, through which the water and the cleaning and polishing products may migrate to the interior of the samples, contributing to the degradation of the polymer. The error associated to the different calculations does not allow to draw conclusions regarding the comparison of the different treatments tested. It is important to underline that besides all the factors that can influence this highly sensitive technique (any small variation of temperature occurring in the detector or in the chromatographic columns' oven, solvent pressure, etc.) the sampling for this technique was done manually and is difficult to assure that goes always to the same depth, and so that the samples are always equivalent. In addition, the heterogeneity of the nacreous samples has probably contributed to the error observed, since is much higher than the error associated with the analysis of the transparent samples.

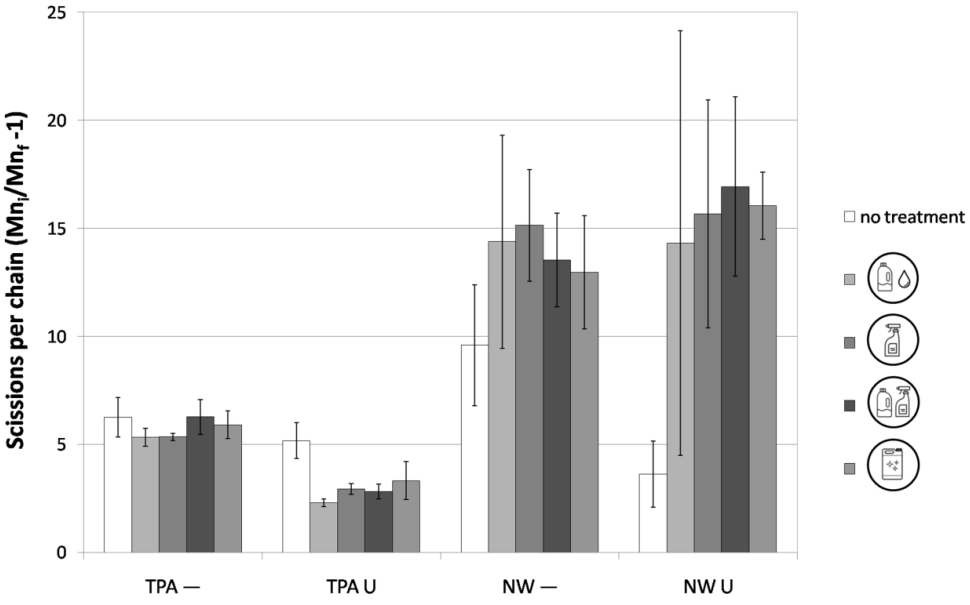


Figure 7.5: Average number of scissions per chain for all PMMA test samples after 4000 h of artificial ageing.

Table 7.4: Weight average molecular weight (M_w) and polydispersity ($Đ_M$) obtained for the test samples. All values result from the average of the values obtained in two different SEC injections of two different collected samples.

Sample	M_w	$Đ_M$
TPA/ 0h	1.44×10^6	2.4
TPA/ 4000h	1.78×10^5	2.2
TPA/1	1.72×10^5	1.8
TPA/2	1.74×10^5	1.9
TPA/3	1.49×10^5	1.8
TPA/4	1.63×10^5	1.9
TPAU 0h	1.34×10^6	2.6
TPAH 4000h	1.79×10^5	2.1
TPAU1	3.21×10^5	2.1
TPAU2	2.69×10^5	2.1
TPAU3	2.62×10^5	2.0
TPAU4	2.19×10^5	1.9
NW/ 0h	5.92×10^5	3.9
NW/ 4000h	5.35×10^4	3.4
NW/1	2.29×10^4	2.2
NW/2	2.37×10^4	2.4
NW/3	2.08×10^4	2.0
NW/4	2.24×10^4	2.0
NWU 0h	5.54×10^5	3.6
NWH 4000h	9.08×10^4	2.7
NWU1	1.99×10^4	2.0
NWU2	1.75×10^4	1.9
NWU3	1.64×10^4	1.9
NWU4	1.84×10^4	2.0

7.4 Conclusions

In this work, treatments for cleaning and polishing PMMA sheets were tested, following the procedure described by Lourdes Castro. Table 7.5 resumes the main alterations observed in the PMMA testing samples.

All treatments tested produced new scratches and left deposits on the samples surface, except for treatment 1 (water+detergent). However, immediately after treatment, no other significant alterations were detected with the analytical techniques used in this research.

Table 7.5: Resume of the alterations observed for the different tested treatments.

Alterations				
optical	Immediately: minor scratches in both TPA and NW.	Immediately: partially disguised original scratches but created new ones; residues. Ageing: promoted cracks on NW surfaces.		Immediately: eliminated original scratches but created new ones; residues Ageing: may have promoted cracks on NW surfaces
physical	n.c.	n.c.	n.c.	n.c.
chemical	For all samples, Ageing: reduced chain scission on TPA thermoformed samples; increased chain scission on NW plane and thermoformed samples.			

n.c.= not conclusive

Before addressing the long-term effect of the treatments, it is important to note that all the historical nacreous white samples (NW), showed more alterations during artificial ageing than the more recent transparent ones (TPA), regardless of whether they had or had not been subjected to thermoforming or to the tested treatments. This was not surprising since these samples had already 50 years of natural ageing in an uncontrolled environment. Furthermore, the different vulnerability of the samples to ageing is also related with the industrial processes and materials used to produce these acrylic sheets, and further research is ongoing to understand the influence of these different factors on the ageing of PMMA. Nevertheless, one of the questions that this work tried to answer was if the treatments under testing would have similar long-term impact on these different types of acrylics. In general, none of the treatments seemed to influence significantly the ageing of the TPA samples. However, on the NW samples, all treatments seemed to increase degradation during ageing (more micro-cracks on samples treated with Altuglas Cleaner, and an increase in chain scissions in all treated samples). These nacreous samples are very particular and became extremely altered during the artificial ageing (even the untreated ones), and so, this tendency might not correspond to what would happen in a real situation. Nevertheless, we may conclude that the impact of the treatments is not independent of the particularities of the acrylic sheet under testing, and therefore, further research in this field should consider this point.

Regarding the assessment of possible differences in the impact of the treatments on the thermoformed versus untransformed samples, it is more difficult to draw any conclusions since some of the results seem to be contradictory and analysis of these samples posed several practical challenges.

Regarding the impact of the different treatments, it was hard to detect differences between them since these are probably very subtle and not clearly detectable by the techniques used.

8 General Conclusions

The main aim of the research developed within the framework of this doctoral thesis was to contribute to the preservation of artworks in acrylic sheet. For that, a holistic approach was adopted, covering the study of the industrial production of the material, its use and transformation by the artists, its degradation, and its active conservation. This approach was necessarily multi and trans disciplinary; it included historical research, material characterization, photodegradation studies, and testing cleaning and polishing conservation procedures. This thesis proves that the knowledge thus obtained is more than the sum of the different parts.

Regarding the industrial production of acrylic sheet, this work shows that acrylic cast sheet was produced in Portugal between 1955 and 2009 and, apparently, at least four companies were in operation during the 1960s: Luso-Sintética, Plásticos do Sado, Ipacril and Socril. With the exception of Socril (later named Paraglas), the core business of these companies was, at their origin, to produce nacreous PMMA sheets from recovered monomer obtained by depolymerization of acrylic residues. This study presents an important contribution to the history of plastics industry in Portugal, a field that has been receiving growing attention in the last years.[17]

This work also gives a significant contribution to the comprehension of the use of acrylic sheet by Portuguese artists, both by the study of the work of Lourdes Castro and Ângelo de Sousa, chosen as case-studies, as well as by the survey conducted in the main modern and contemporary art collections in the country. The analysis of the case-studies revealed how different aspects of this "new material'' attracted the artists. Lourdes Castro was mainly interested in its transparency and in the ways it transmits light and

[17]As shown by the FCT-MCTES financed project "O Triunfo da Baquelite - Contributos para uma História dos Plásticos em Portugal" (PTDC/IVC-HFC/5174/2014) and the recent exhibition at Museu de Leiria "Plasticidade – Uma História dos Plásticos em Portugal".

projects shadows; one may say that the focus was in the final effect of the artwork. On the contrary, Ângelo de Sousa was more concerned with exploring the PMMA thermoplastic properties, or in the possibilities of creating three-dimensional forms unachievable with the traditional materials; in his case, the focus was mainly on the process. Understanding these particularities is fundamental when considering conservation strategies for their artworks. From a broader perspective, the results of the survey present an overview of the use of this material by artists. The results show that acrylic sheet is a material used by the Portuguese artists at least since the 1960s to the present day, and that no less than 48 Portuguese authors have used it somehow in their artworks. The artworks surveyed included paintings, sculptures, objects/reliefs, photography, installations and even artist books, which reveals the diversity of uses that artists have given to PMMA.

One of the main goals of this research was to understand the influence of the *origin* of the PMMA sheets in their long-term stability, more precisely, to assess the impact of different formulations and industrial production processes on the properties and susceptibility of PMMA cast sheets to photooxidation. The results obtained in this research show that equivalent PMMA cast sheets produced by different companies in the same period (2000s) presented different properties such as molecular weight distribution, surface hardness, or thermal behaviour. Differences were also observed in the behaviour of the samples during artificial ageing in the degree of scissions per chain, surface hardness alteration, thermal degradation, UV fluorescence, and physical stability. Poorer performances were correlated with the presence of more plasticizer in the composition of the material and more defects in the polymeric structure due to use of recycled monomer and the lack of a post polymerization step. The presence of the inorganic pigment cadmium red, Cd(S,Se), was also assessed and did not seem to influence the initial properties of the PMMA sheets, but might have a protective effect during photodegradation, as seen by SEC analysis and micro-hardness measurements. Surprisingly, major differences between reference samples from 2000s and historical artist's samples from 1960s were not detected. Therefore, it can be concluded that the global production process (which may include the polymerization conditions, the monomer origin and/or the organic additives added) plays a more important role in the properties and photostability of PMMA cast sheets than the presence of cadmium red, or the production decade of the acrylic sheets. This research shows that the most relevant characterization methods for assessing intrinsic properties of PMMA to help estimating their photostability were size exclusion chromatography, micro-indentation, thermogravimetry, and thermodesorption-gas chromatography/mass spectrometry. The

results obtained underline the importance of characterizing the material beyond polymer identification for understanding the ageing behaviour of a plastic object.

In this line, another important contribution of this thesis is the identification, through Raman microspectroscopy, of plumbonacrite and bismuth oxychloride as the pigments responsible for the pearlescent effect on the acrylic sheets of Ângelo de Sousa. It was the first time that these effect pigments were identified in-situ in historical plastics. Even though the alteration mechanism that led to the darkening of plumbonacrite in the PMMA matrix during artificial ageing was not completely understood, its accurate identification is the necessary first step for following that research.

A correlation between the condition of the acrylic sheets used in the artworks and their *origin* or specific characteristics (e.g. colour, transparency, or thickness) was not detected during the survey. In fact, most of the artworks surveyed and their PMMA elements were in good or fair condition, and, as expected, the main problems observed were dust and dirt deposits, abrasion, and scratches, which are mainly related with extrinsic factors such as inappropriate housing, handling and cleaning, and eventual accidents. Nevertheless, the relevance of the intrinsic factors considered in this thesis for the conservation of PMMA artifacts was shown through the testing of the treatments for cleaning and polishing. The results obtained illustrate that the impact of the treatments is not independent of the particularities of the acrylic sheet. Regarding the samples studied, recent (2000s), transparent samples, from Paraglas (produced with new monomer and a post-polymerization step) did not show significant differences between treated and untreated samples after ageing. On the contrary, in old (1960s) nacreous samples, from Plásticos do Sado (produced with recycled monomer, more additives, and without a post-polymerization step), all treated samples presented more degradation signs during ageing than untreated ones. This work shows clearly that not all cast acrylic sheets are alike and that this should be considered when testing conservation treatments.

A limitation of this study was related with the use of historical or commercial samples of acrylic sheet, in opposition to laboratory prepared samples. If on the one hand they are closer to the reality found in artworks, on the other hand, their composition details are partially unknown and they may have already suffered some kind of natural ageing. This hinders a complete understanding of the degradation mechanisms involved. Nevertheless, this thesis offers some insight to the possible intrinsic factors that may influence the stability of PMMA and lays groundwork for further research into these influences.

A second limitation was observed in the characterization of thermoformed samples (that simulated the artworks of Ângelo de Sousa). The volume and curvature of these samples made impossible the characterization through many of the techniques used in this study, such as micro-indentation, optical microscopy, and FTIR-ATR. Notwithstanding these limitations, the study of the influence of the technique used by Ângelo de Sousa in the long-term photostability of acrylic sheet is ongoing, with a focus on the action of heating the PMMA. Nevertheless, further work on ways to assess alterations in non-planar samples is necessary.

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Appendix I – Supplementary data to Chapter 3

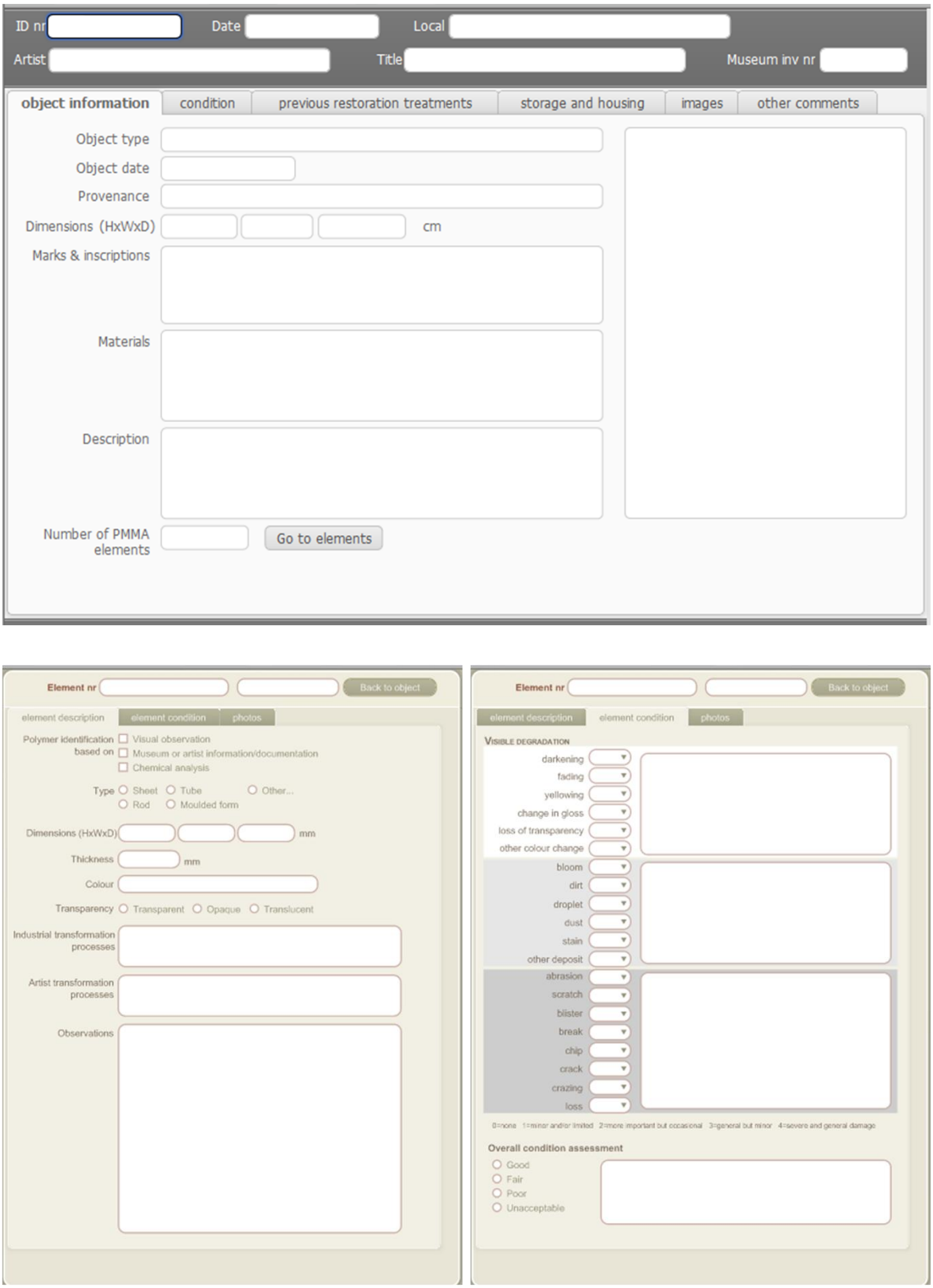
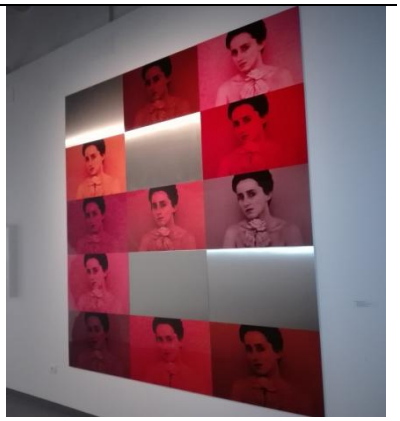
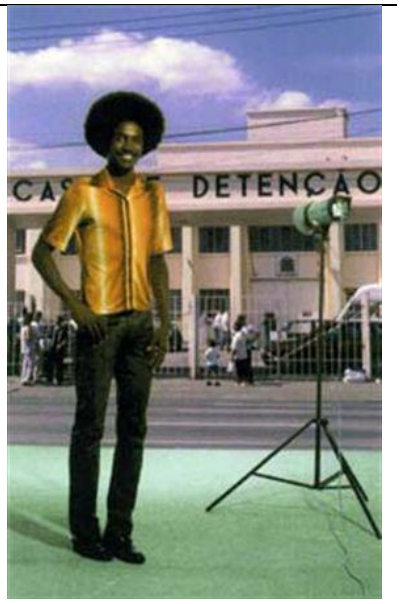
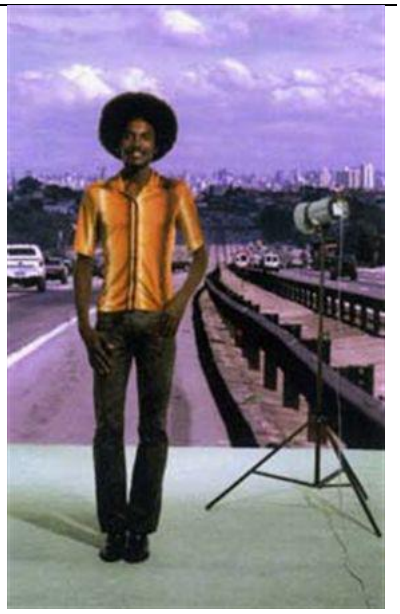
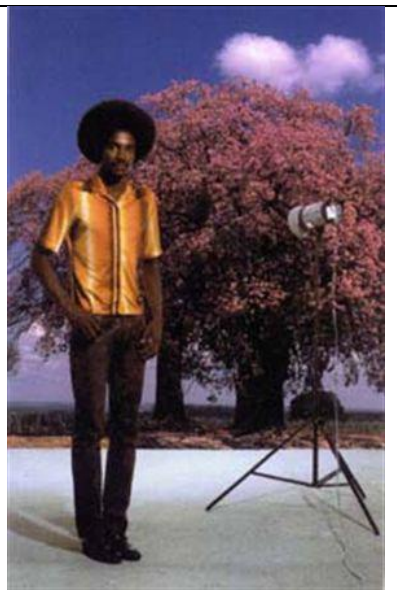


Figure A1.1: Layouts for records in the *artworks table* and *elements table* in the survey database.

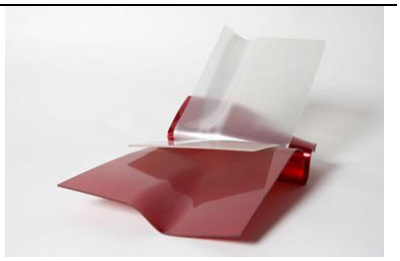
Table A1.1: Artworks examined during the survey.

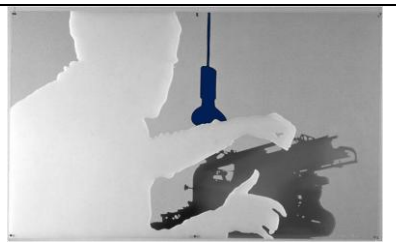
ID nr	Artist	Object type	Date	Colection	
1	Julia Ventura (Lisboa, 1952)	Photography	1989	CGD	
2	Caio Reisewitz (São Paulo, 1967)	Photography	2001	CGD	
3	Caio Reisewitz (São Paulo, 1967)	Photography	2001	CGD	

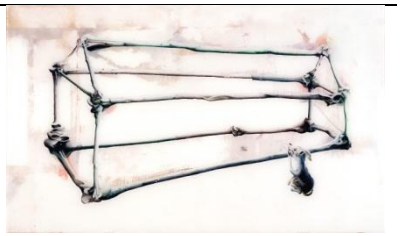
4	Caio Reisewitz (São Paulo, 1967)	Photography	2001	CGD	
5	Caio Reisewitz (São Paulo, 1967)	Photography	2001	CGD	
6	Lourdes Castro (Funchal, 1930)	Painting	1965	CGD	

7	Manuela Almeida	Object/Relief	1990	CGD	
8	Fernando Alvim (Luanda, 1963)	Object/Relief	2003	CGD	
9	René Bertholo (Alhandra, 1935 – V. N. de Cacela, 2005)	Sculpture	1974	CGD	
10	Ana Vidigal (Lisboa, 1960)	Object/Relief	2002	CGD	

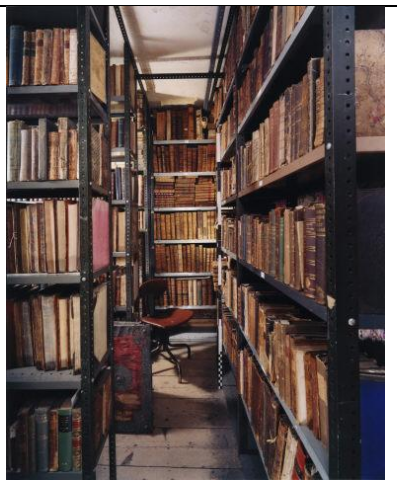
11	Ana Vidigal (Lisboa, 1960)	Object/Relief	2002	CGD	
12	Ana Vidigal (Lisboa, 1960)	Object/Relief	2002	CGD	
13	Lourdes Castro (Funchal, 1930)	Object/Relief	1967	MB	

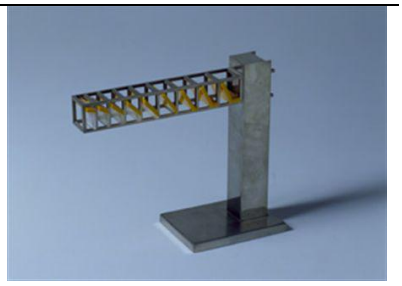
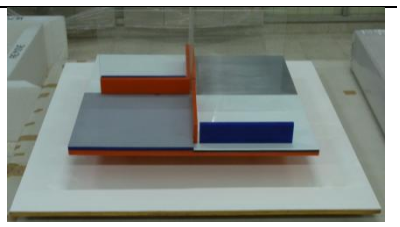
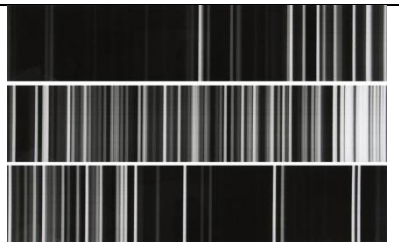
14	Arman (Nice, 1928 - New York 2005)	Sculpture	1971	MB	
15	Ângelo de Sousa (Lourenço Marques 1938 - Porto 2011)	Sculpture	1965	CAM-FCG	
16	Lourdes Castro (Funchal, 1930)	Object/Relief	1964	CAM-FCG	
17	João Vieira (Vidago, 1934 - Lisboa, 2009)	Object/Relief	1971	CAM-FCG	

18	Lourdes Castro (Funchal, 1930)	Object/Relief	1968	CAM-FCG	
19	Lourdes Castro (Funchal, 1930)	Object/Relief	1965	CAM-FCG	
20	Hein Semke (Hamburgo, 1899 - Lisboa, 1995)	Object/Relief	1971	CAM-FCG	
21	Hein Semke (Hamburgo, 1899 - Lisboa, 1995)	Object/Relief	1971	CAM-FCG	
22	Hein Semke (Hamburgo, 1899 - Lisboa, 1995)	Object/Relief	1971	CAM-FCG	

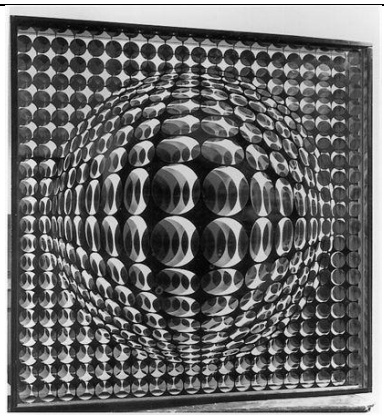
23	Hein Semke (Hamburgo, 1899 - Lisboa, 1995)	Object/Relief	1971	CAM-FCG	
24	Hein Semke (Hamburgo, 1899 - Lisboa, 1995)	Object/Relief	1971	CAM-FCG	
25	Gil Heitor Cortesão (Lisboa, 1967)	Painting	1998	CAM-FCG	
26	Gil Heitor Cortesão (Lisboa, 1967)	Painting	1998	CAM-FCG	
27	Gil Heitor Cortesão (Lisboa, 1967)	Painting	2004	CAM-FCG	
28	Renée Gagnon (Montreal 1942)	Painting	1985	CAM-FCG	

29	Peter Blake (Dartford, 1932)	Object/Relief	1961	CAM-FCG	
30	Mary Martin (Folkstone,1907-London,1969)	Object/Relief	1959	CAM-FCG	
31	Anthony Hill (London, 1930)	Object/Relief	1963	CAM-FCG	
32	René Bertholo (Alhandra, 1935 — V. N. de Cacela, 2005)	Object/Relief	1967	CAM-FCG	

33	Jane & Louise Wilson (Newcastle upon Tyne 1967)	Photography	2008	CAM-FCG	
34	Jane & Louise Wilson (Newcastle upon Tyne, 1967)	Photography	2009	CAM-FCG	
35	Júlia Ventura (Lisboa, 1952)	Photography	1987	CAM-FCG	
36	Armando Ferraz (Lisboa 1968)	Photography	2000	CAM-FCG	

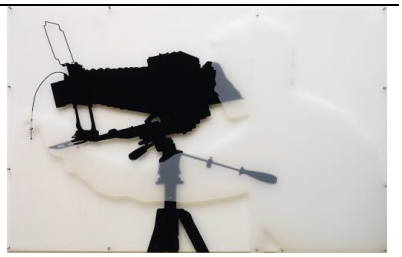
37	Ângela Ferreira (Lourenço Marques, 1958)	Instalation	1997	CGD	
38	Artur Rosa (Lisboa, 1948)	Sculpture	1973	CGD	
39	Ana Vieira (Coimbra, 1940 – Lisboa, 2016)	Object/Relief	1993	CGD	
40	Gillian Wise (Londres, 1936)	Object/Relief	1964	CAM-FCG	
41	José Luís Neto (Sátão, 1966)	Photography	2005	CAM-FCG	

42	José de Guimarães (Guimarães, 1939)	Sculpture	1983	CAM-FCG	
43	José de Guimarães (Guimarães, 1939)	Sculpture	1983	CAM-FCG	
44	José de Guimarães (Guimarães, 1939)	Sculpture	1983	CAM-FCG	

45	José de Guimarães (Guimarães, 1939)	Sculpture	1983	CAM-FCG	
46	José de Guimarães (Guimarães, 1939)	Sculpture	1983	CAM-FCG	
47	Augusto Alves da Silva (Lisboa, 1963)	Photography	2011	CAM-FCG	
48	Victor Vasarely (Pecs, 1908 - Paris, 1997)	Painting	1973	MNAC	

49	Eduardo Nery (Figueira da Foz, 1938 - Lisboa 2013)	Painting	1967	MNAC	
50	Miguel Leal (Porto, 1967)	Instalation	2001	MNAC	
51	Lourdes Castro (Funchal, 1930)	Object/Relief	1965	MNAC	
52	Eduardo Nery (Figueira da Foz, 1938 - Lisboa, 2013)	Painting	1967	MNAC	
53	Ângela Ferreira (Lourenço Marques, 1958)	Instalation	19932 006	MNAC	

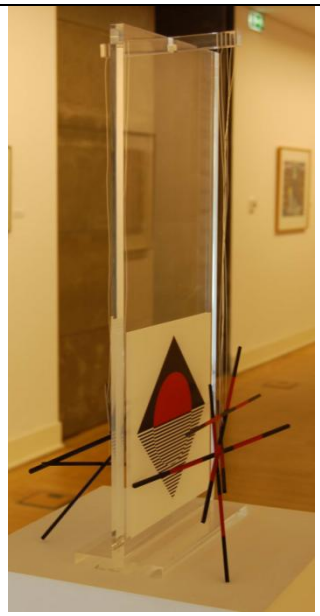
54	Lourdes Castro (Funchal, 1930)	Object/Relief	1965	MNAC	
55	Julia ventura (Lisboa, 1952)	Photography	1987	MNAC	
56	Júlia Ventura (Lisboa, 1952)	Photography	1987	MNAC	
57	Julia Ventura (Lisboa, 1952)	Photography	1987	MNAC	
58	Lourdes Castro (Funchal, 1930)	Object/Relief	1968	Serralves	

59	Lourdes Castro (Funchal, 1930)	Painting	1965	Serralves	
60	E. M. de Melo e Castro (Covilhã 1932)	Sculpture	19672 005	Serralves	 
61	Lourdes Castro (Funchal, 1930)	Book	1971	Serralves	
62	António Costa Pinheiro (Moura 1932 - Munique 2015)	Sculpture	1971	Serralves	
63	Lourdes Castro (Funchal, 1930)	Object/Relief	1967	Serralves	

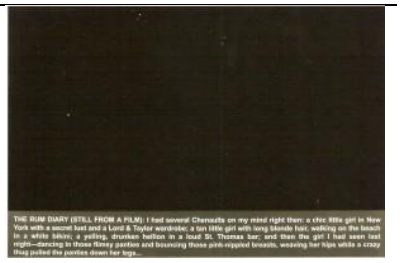
64	Ana Harthely (Porto 1929 - Lisboa 2015)	Sculpture	1960	Serralves	
65	José Rodrigues (Luanda 1936 - Porto 2016)	Sculpture	1971	Serralves	
66	João Vieira (Vidago 1934 - Lisboa 2009)	Sculpture	1971	Serralves	 
67	Lourdes Castro (Funchal 1930)	Object/Relief	1967	Serralves	

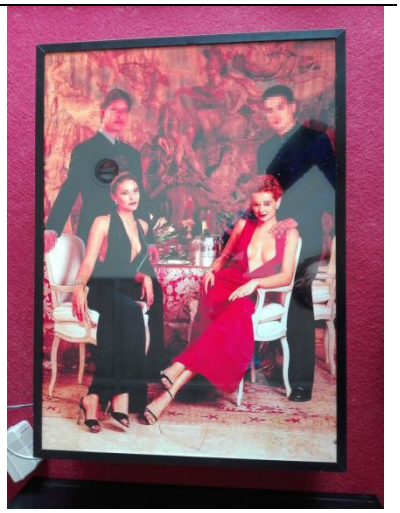
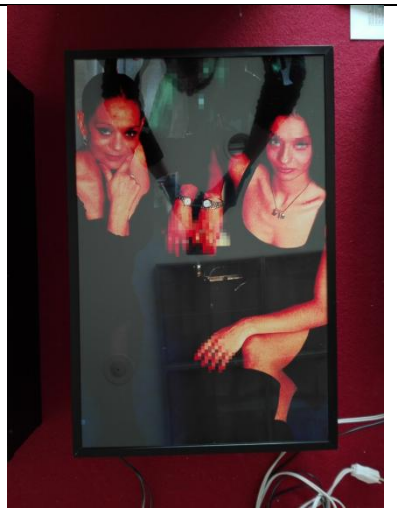
68	Jorge Pinheiro (Coimbra 1931)	Sculpture	1971	CAMB	
69	Lourdes Castro (Funchal 1930)	Painting	1965	CAMB	
70	Lourdes Castro (Funchal 1930)	Painting	1965	CAMB	

71	Lourdes Castro (Funchal 1930)	Object/Relief	1968	CAMB	
72	René Bertholo (Alhandra 1935 — V. N. de Cacela 2005)	Sculpture	1971	CAMB	
73	René Bertholo (Alhandra 1935 — V. N. de Cacela 2005)	Sculpture	1972	CAMB	

74	Jésus-Rafael Soto (Ciudad Bolívar 1923 - Paris 2005)	Sculpture	1991	CAMB	
75	Arman (Nice 1928 - Nova Iorque 2005)	Sculpture	1991	CAMB	
76	Augusto Alves da Silva (Lisboa 1963)	Photography	2003	MACE	

77	Edgar Martins (Évora 1977)	Photography	2008	MACE	
78	João Paulo Feliciano (Caldas da Rainha 1963)	Instalation	2005	MACE	
79	Gil Heitor Cortesão (Lisboa 1967)	Painting	2001	MACE	
80	Gil Heitor Cortesão (Lisboa 1967)	Painting	2001	MACE	

81	Nuno Silva	Sculpture	2000	MACE	
82	Ângela Ferreira (Maputo 1958)	Instalation	1993	MACE	
83	Rui Toscano (Lisboa 1970)	Object/Relief	1996	MACE	
84	João Louro (Lisboa 1963)	Painting	20092 011	MACE	

85	José Maçãs de Carvalho (Anadia 1960)	Object/Relief	1998	MACE	
86	José Maçãs de Carvalho (Anadia 1960)	Object/Relief	1998	MACE	
87	José Maçãs de Carvalho (Anadia 1960)	Object/Relief	1998	MACE	

88	José Maçãs de Carvalho (Anadia 1960)	Object/Relief	1998	MACE	
89	José Maçãs de Carvalho (Anadia 1960)	Object/Relief	1998	MACE	

Appendix II – Supplementary data to Chapter 4

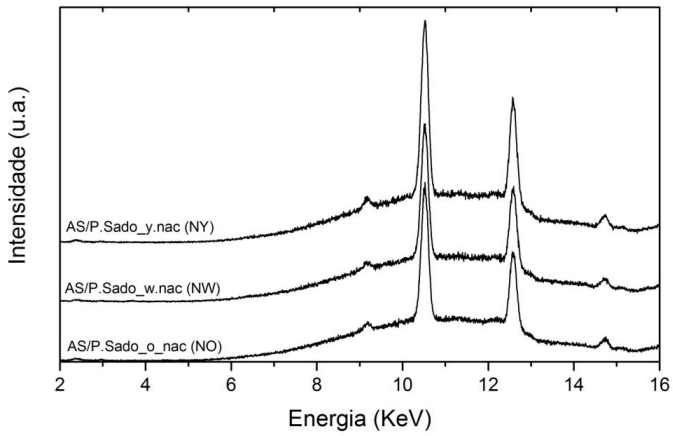


Figure A2.1: XRF spectra of Ângelo de Sousa's nacreous samples.

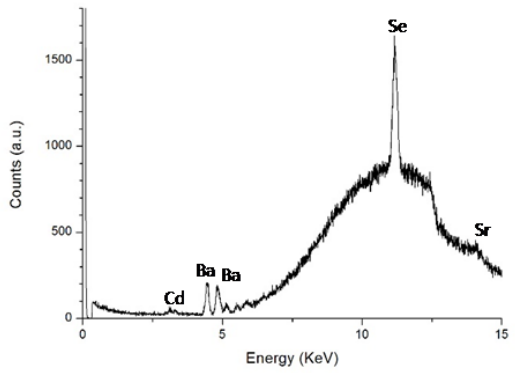


Figure A2.2: XRF spectrum of red sample LC/Altuglas (RAL)

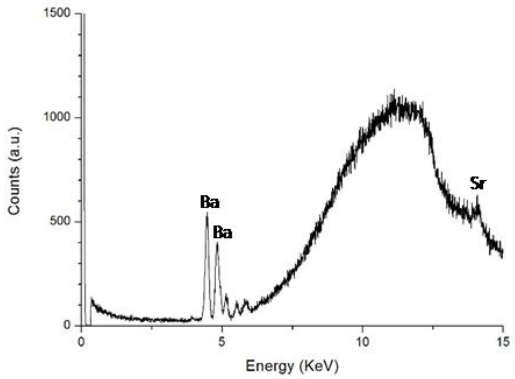


Figure A2.3: XRF spectrum of red sample Paraglas_6470

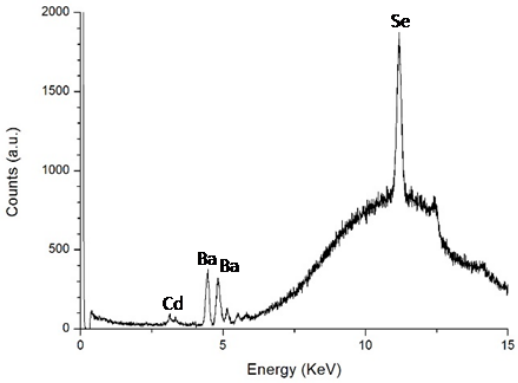


Figure A2.4: XRF spectrum of red sample P.Sado_9081 (RPS)

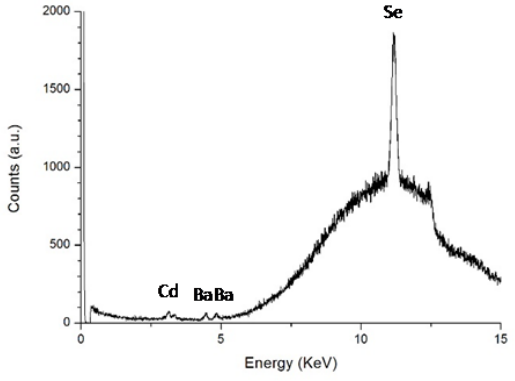


Figure A2.5: XRF spectrum of red sample Paraglas_6500 (RPA)

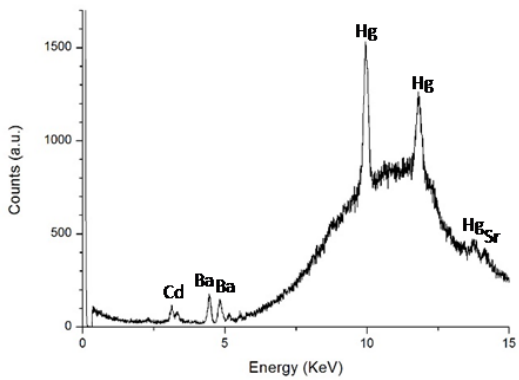


Figure A2.6: XRF spectrum of red sample P.Sado_9082

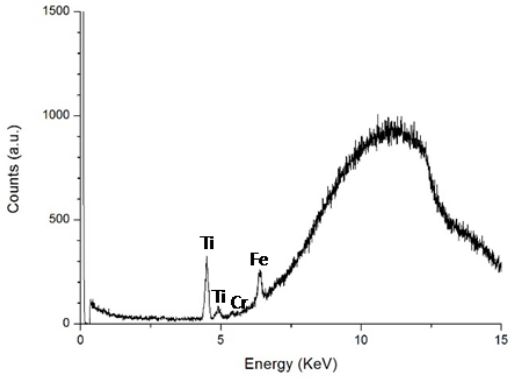
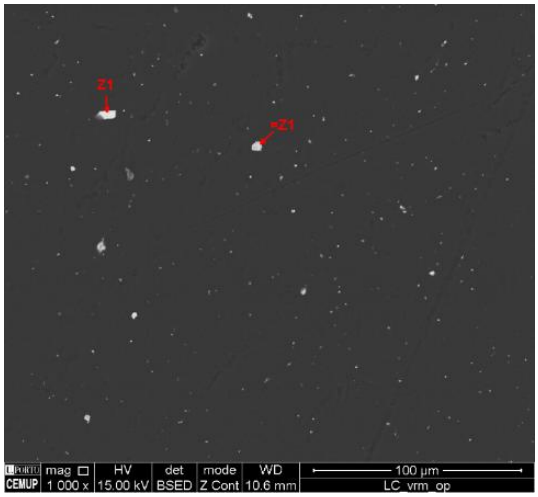
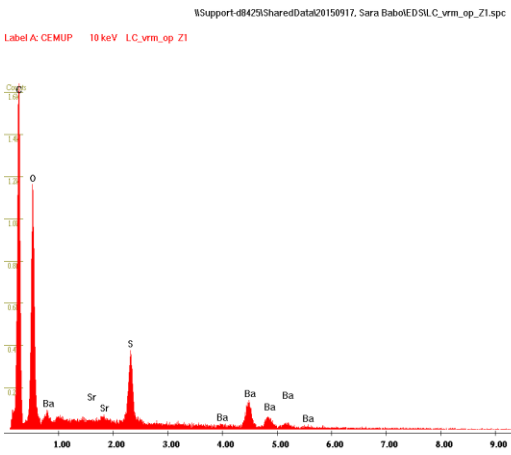
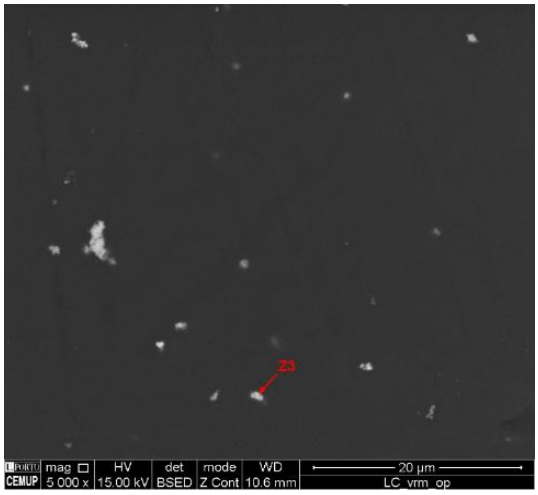


Figure A2.7: XRF spectrum of red sample Paraglas_6700







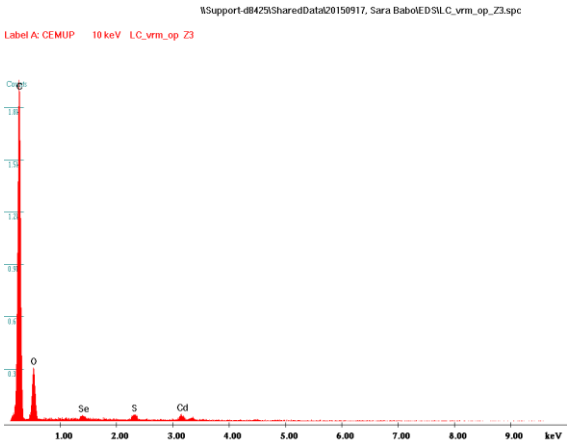


Figure A2.8: SEM-EDS results for red sample LC/Altuglas (RAL).

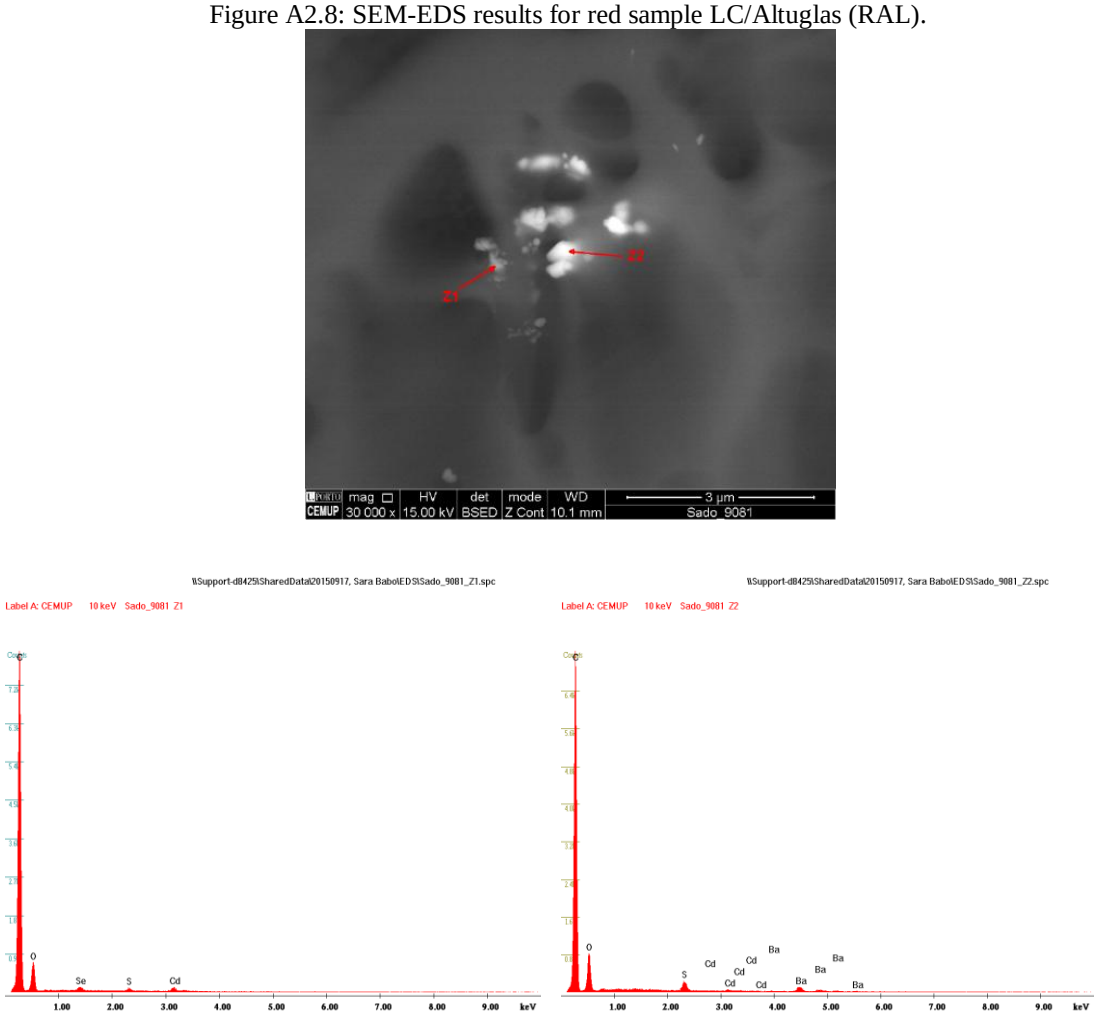


Figure A2.9: SEM-EDS results for red sample P.Sado_9081 (RPS).

Appendix III – Supplementary data to Chapter 5

Transmission spectra of the filter used in the solarbox

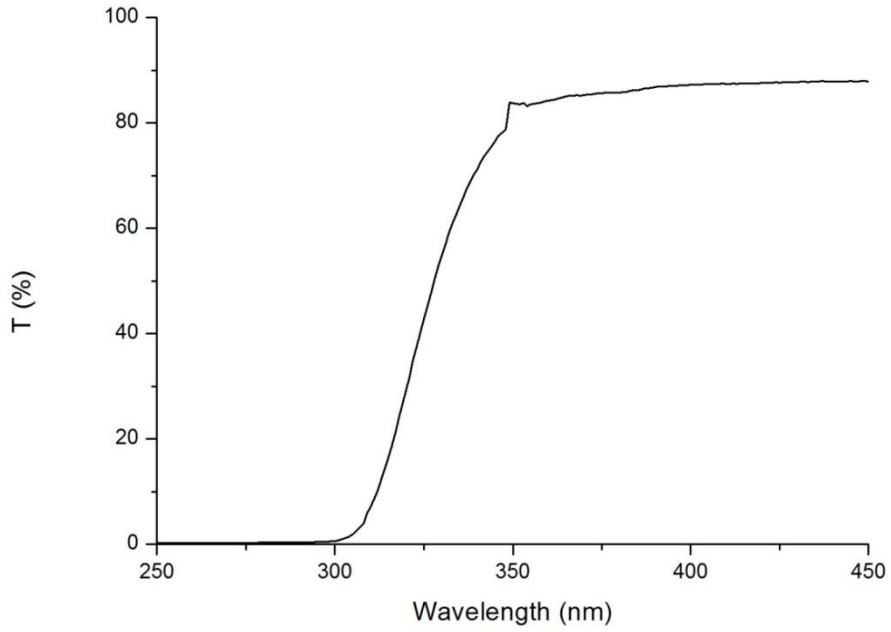


Figure A3.1: UV-Vis transmission spectrum of the filter used in the solarbox during the artificial ageing experience.

Data from the photodegradation experience

Gravimetry results
FTIR-ATR spectra
Raman spectra
UV-Vis spectra
Colorimetry results
OM images
Vickers Hardnes results

Table A3.1: Gravimetry results from TPA, TPS, TPL, RPA, RPS and RAL samples during ageing

	0 h		2000 h		4000 h		6000 h		8000 h		8000 h – 0 h	
	x̄ (g)	σ	x̄ (g)	σ	x̄ (g)	σ	x̄ (g)	σ	x̄ (g)	σ	Δ (g)	total (%)
TPA1	0.78621	0.00003	0.78634	0.00002	0.78483	0.00005	0.78470	0.00010	0.78482	0.00006	-0.00139	
TPA2	0.78968	0.00005	0.78989	0.00001	0.78835	0.00006	0.78824	0.00009	0.78835	0.00009	-0.00133	
TPA3	0.78243	0.00007	0.78260	0.00002	0.78117	0.00004	0.78098	0.00005	0.78105	0.00009	-0.00137	
x̄	**0.78611**	**0.00005**	**0.78628**	**0.00002**	**0.78478**	**0.00005**	**0.78464**	**0.00008**	**0.78474**	**0.00008**	**-0.00136**	**-0.17357**
S1	0.77168	0.00004	0.77283	0.00002	0.77087	0.00008	0.77061	0.00009	0.77043	0.00009	-0.00125	
TPS2	0.81212	0.00005	0.81318	0.00003	0.81124	0.00007	0.81091	0.00007	0.81089	0.00011	-0.00123	
TPS3	0.80365	0.00006	0.80465	0.00001	0.80282	0.00005	0.80244	0.00005	0.80222	0.00009	-0.00144	
x̄	**0.79582**	**0.00005**	**0.79689**	**0.00002**	**0.79498**	**0.00007**	**0.79465**	**0.00007**	**0.79451**	**0.00010**	**-0.00131**	**-0.16405**
TPL1	0.99710	0.00011	0.99679	0.00001	0.99400	0.00006	0.99364	0.00007	0.99333	0.00011	-0.00377	
TPL2	0.98289	0.00006	0.98260	0.00002	0.97987	0.00007	0.97943	0.00008	0.97914	0.00010	-0.00375	
TPL3	0.97326	0.00010	0.97311	0.00002	0.97051	0.00006	0.97000	0.00003	0.96965	0.00010	-0.00361	
x̄	**0.98442**	**0.00009**	**0.98417**	**0.00001**	**0.98146**	**0.00006**	**0.98103**	**0.00006**	**0.98071**	**0.00010**	**-0.00371**	**-0.37687**
RPA1	**0.68674**	**0.00008**	**0.68671**	**0.00003**	**0.68476**	**0.00005**	**0.68463**	**0.00004**	**0.68470**	**0.00005**	**-0.00204**	**-0.29657**
RPS1	**0.67687**	**0.00005**	**0.67721**	**0.00003**	**0.67491**	**0.00003**	**0.67444**	**0.00009**	**0.67398**	**0.00008**	**-0.00289**	**-0.42697**
RAL1	0.68606	0.00006	0.68585	0.00002	0.68375	0.00005	0.68362	0.00008	0.68359	0.00007	-0.00247	
RAL2	0.68464	0.00004	0.68436	0.00002	0.68334	0.00003	0.68217	0.00010	0.68216	0.00011	-0.00248	
RAL3	0.67480	0.00005	0.67455	0.00004	0.67266	0.00003	0.67234	0.00006	0.67244	0.00004	-0.00236	
x̄	**0.68183**	**0.00005**	**0.68159**	**0.00003**	**0.67991**	**0.00004**	**0.67938**	**0.00008**	**0.67940**	**0.00007**	**-0.00244**	**-0.35753**

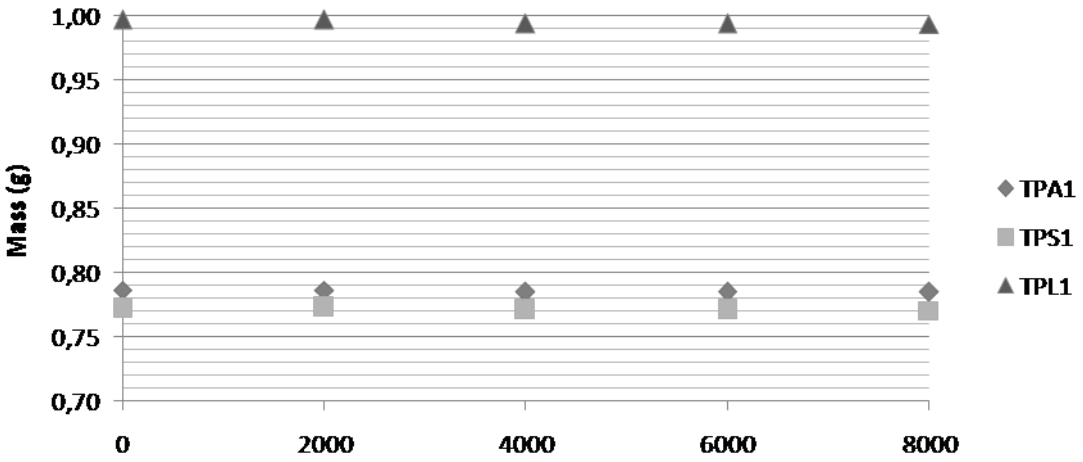


Figure A3.2: Gravimetry results from TPA1, TPS1 and TPL1 samples during ageing.

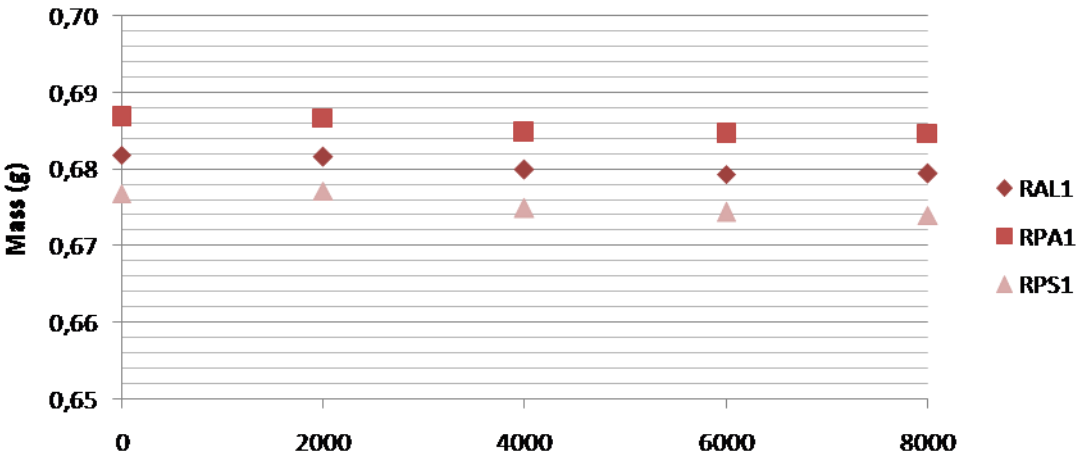


Figure A3.3: Gravimetry results from RPA1, RPS1 and RAL1 samples during ageing.

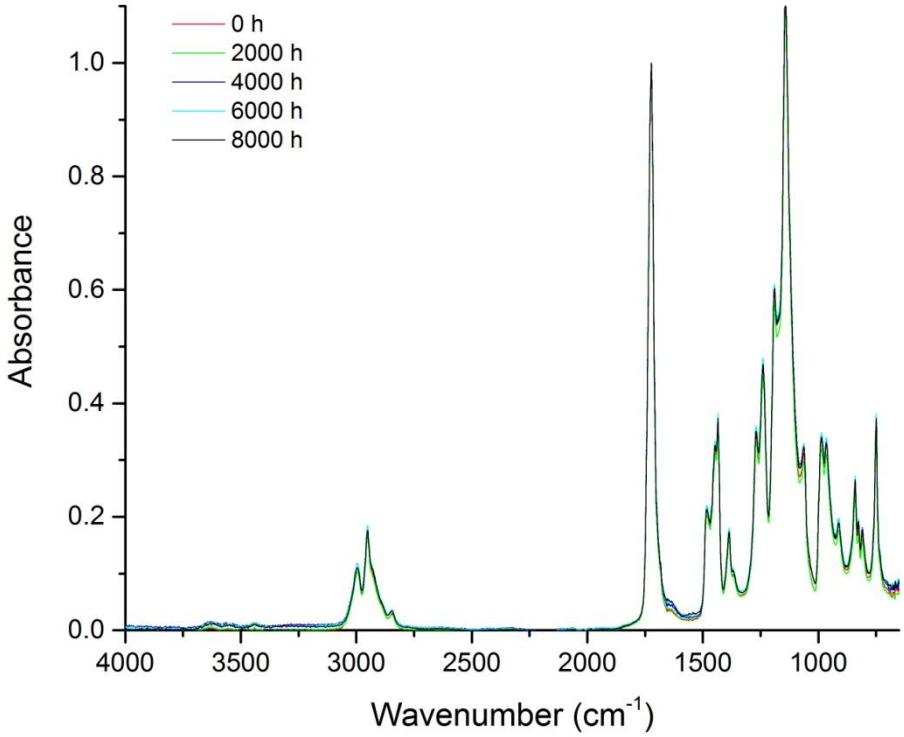


Figure A3.4: Infrared spectra of TPA sample at 0, 2000, 4000, 6000 and 8000 hours.

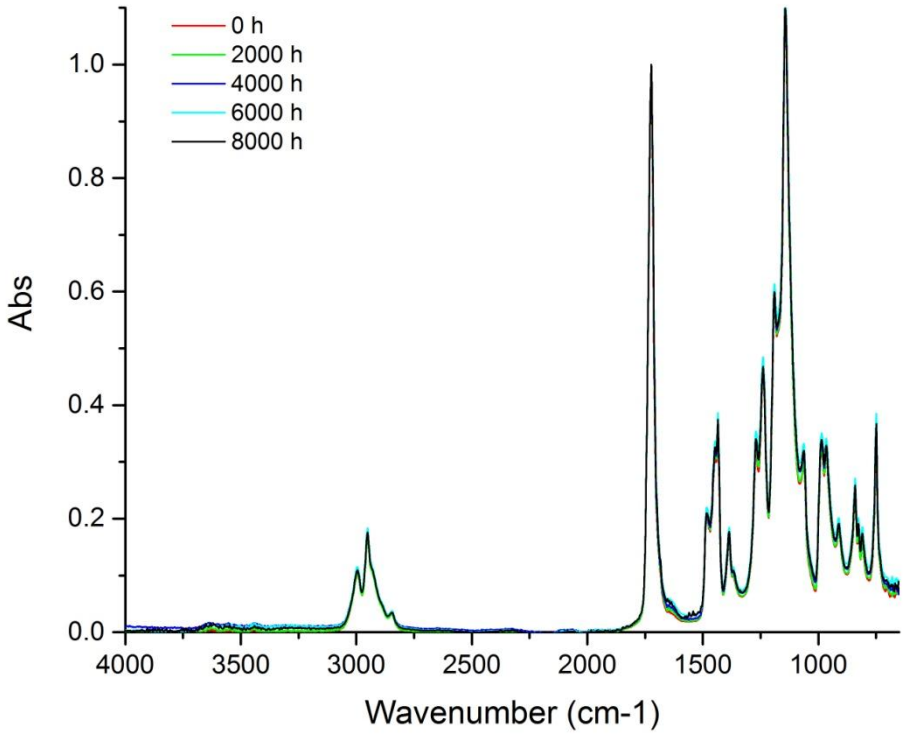


Figure A3.5: Infrared spectra of TPS sample at 0, 2000, 4000, 6000 and 8000 hours.

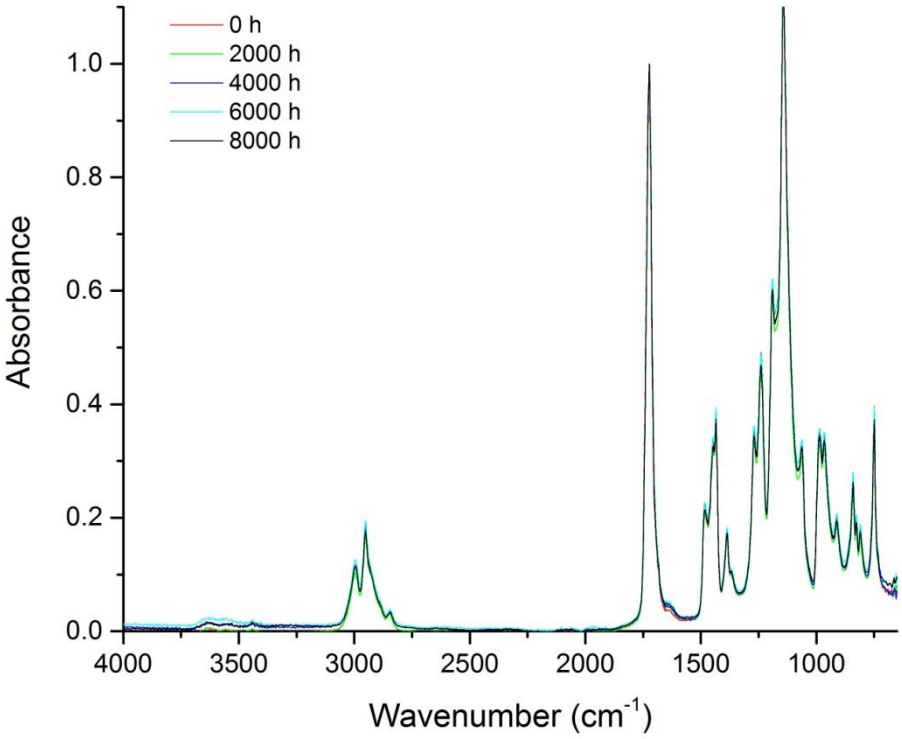


Figure A3.6: Infrared spectra of TPL sample at 0, 2000, 4000, 6000 and 8000 hours.

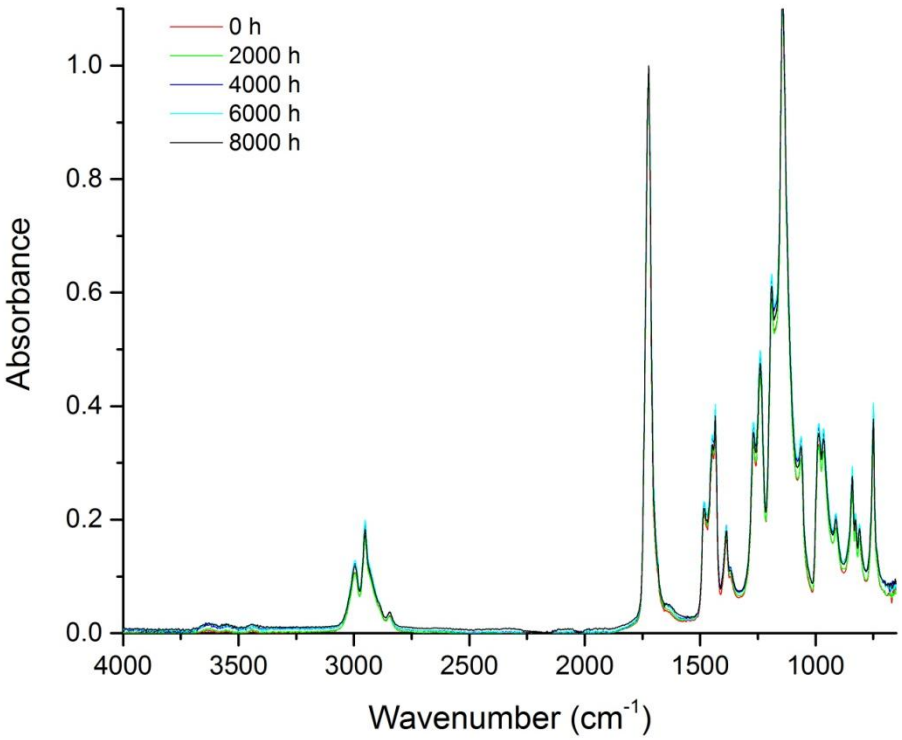


Figure A3.7: Infrared spectra of RPA sample at 0, 2000, 4000, 6000 and 8000 hours.

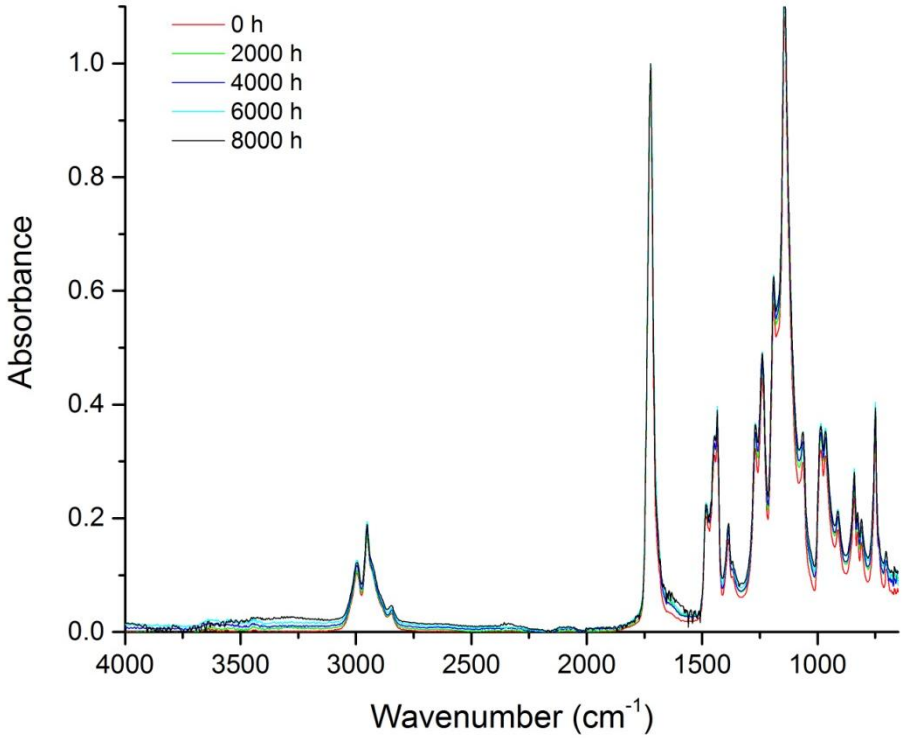


Figure A3.8: Infrared spectra of RPS sample at 0, 2000, 4000, 6000 and 8000 hours.

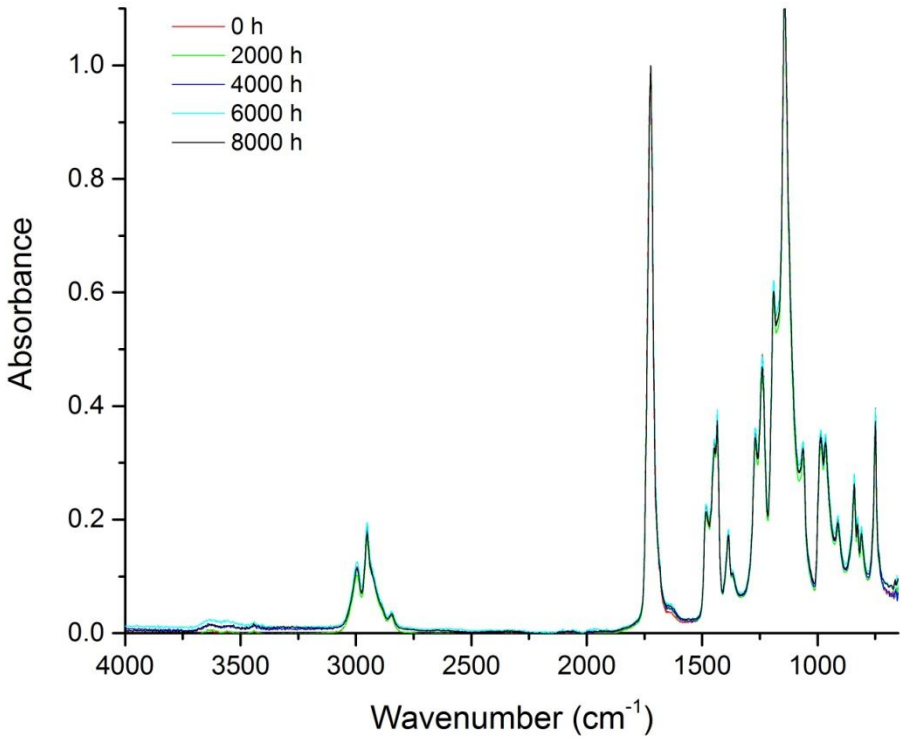


Figure A3.9: Infrared spectra of RAL sample at 0, 2000, 4000, 6000 and 8000 hours.

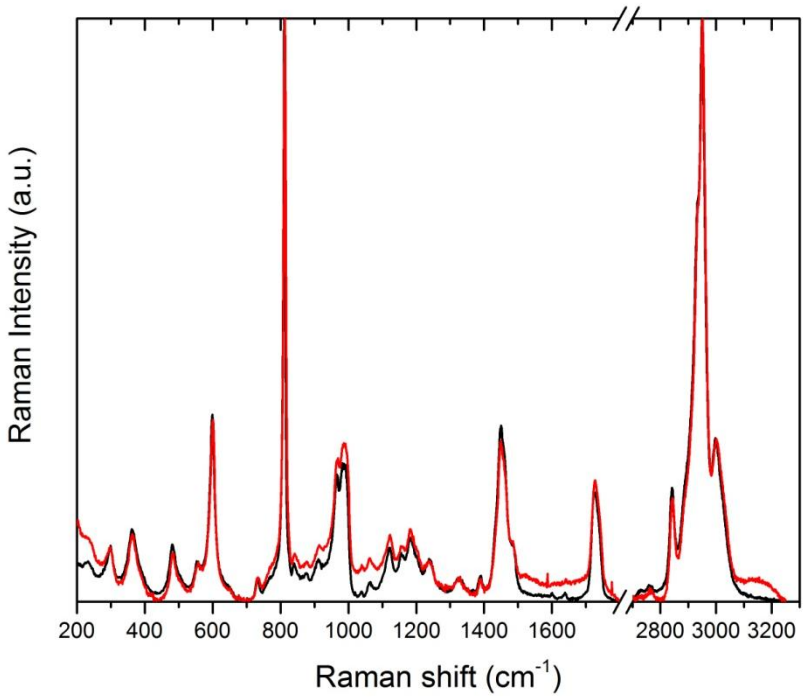


Figure A3.10: Raman spectra of TPA sample before (black line) and after (red line) 8000 h of artificial ageing. Base line was corrected for the 8000 h spectrum and both spectra are normalized.

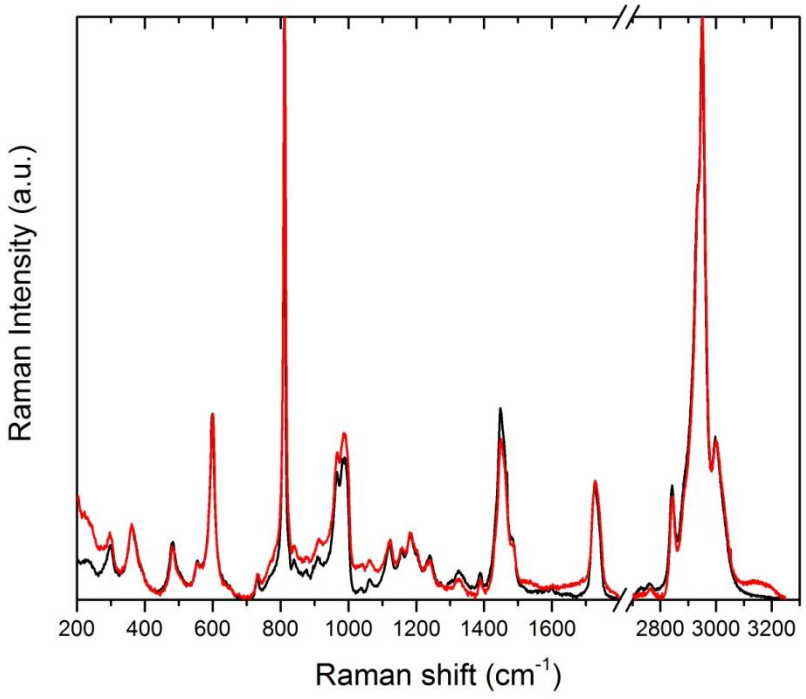


Figure A3.11: Raman spectra of TPA sample before (black line) and after (red line) 8000 h of artificial ageing. Base line was corrected for the 8000 h spectrum and both spectra are normalized.

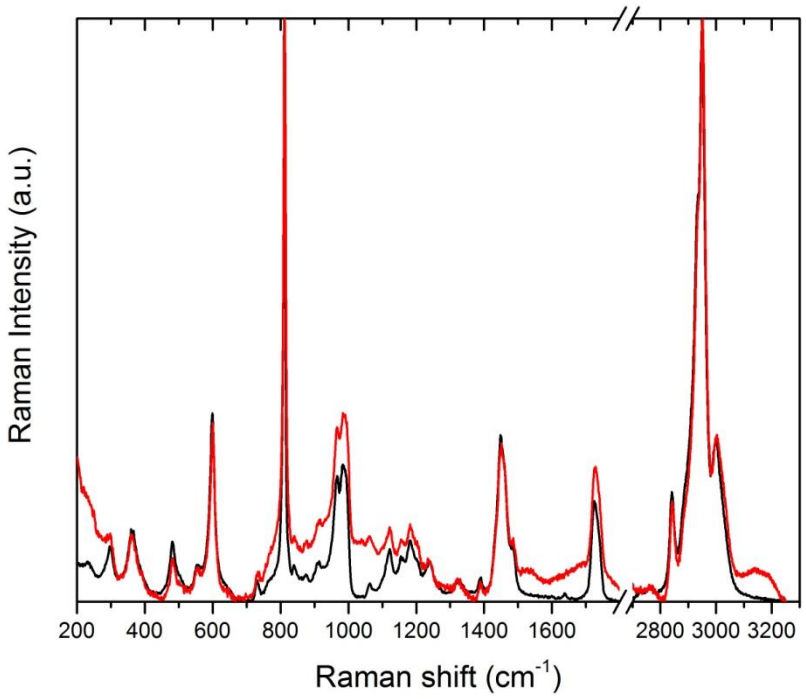


Figure A3.12: Raman spectra of TPL sample before (black line) and after (red line) 8000 h of artificial ageing. Base line was corrected for the 8000 h spectrum and both spectra are normalized.

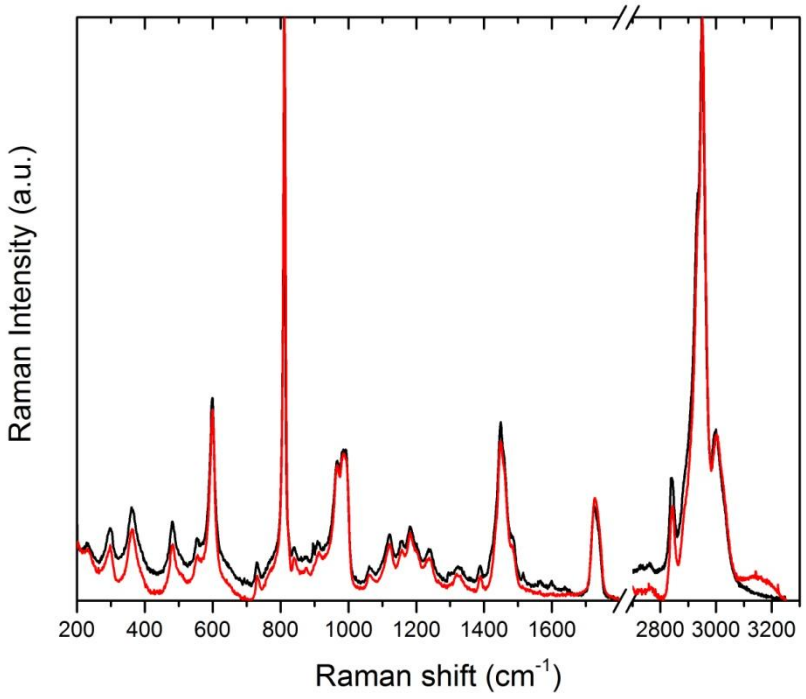


Figure A3.13: Raman spectra of RPA sample before (black line) and after (red line) 8000 h of artificial ageing. Base line was corrected for the 8000 h spectrum and both spectra are normalized.

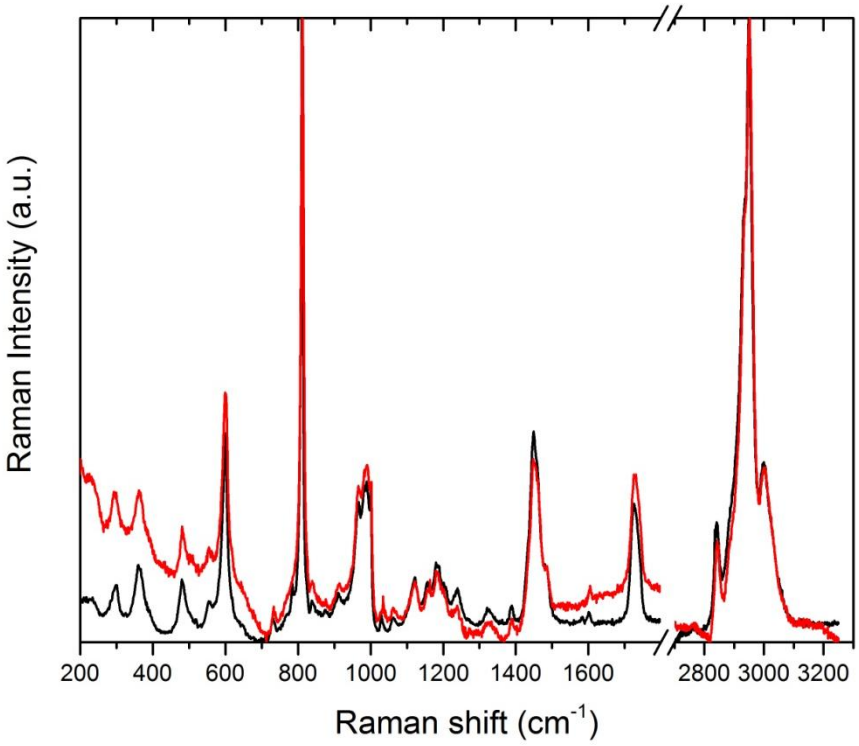


Figure A3.14: Raman spectra of RPS sample before (black line) and after (red line) 8000 h of artificial ageing. Base line was corrected for the 8000 h spectrum and both spectra are normalized.

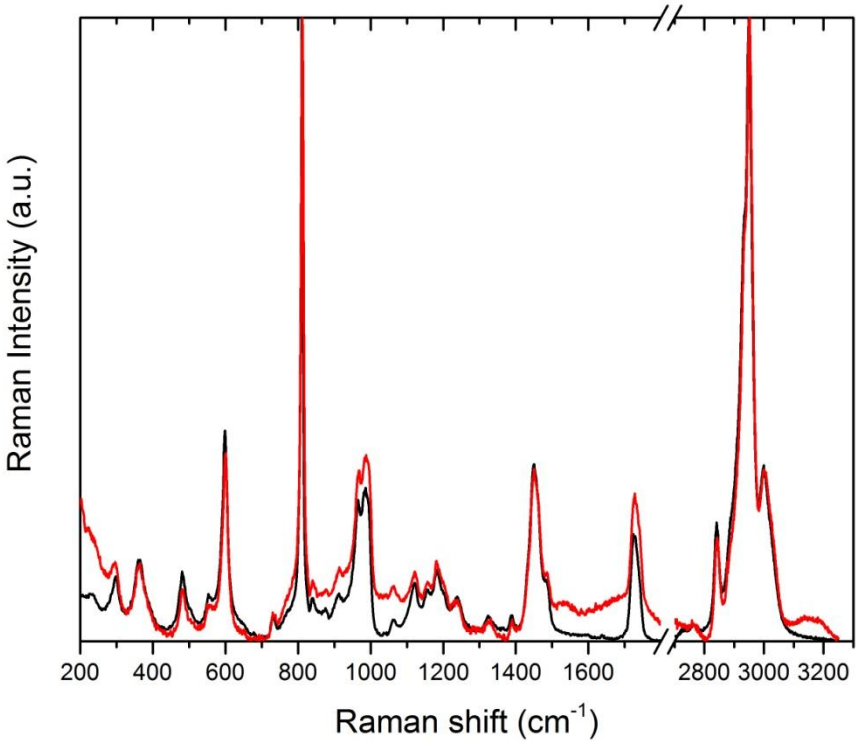


Figure A3.15: Raman spectra of RAL sample before (black line) and after (red line) 8000 h of artificial ageing. Base line was corrected for the 8000 h spectrum and both spectra are normalized.

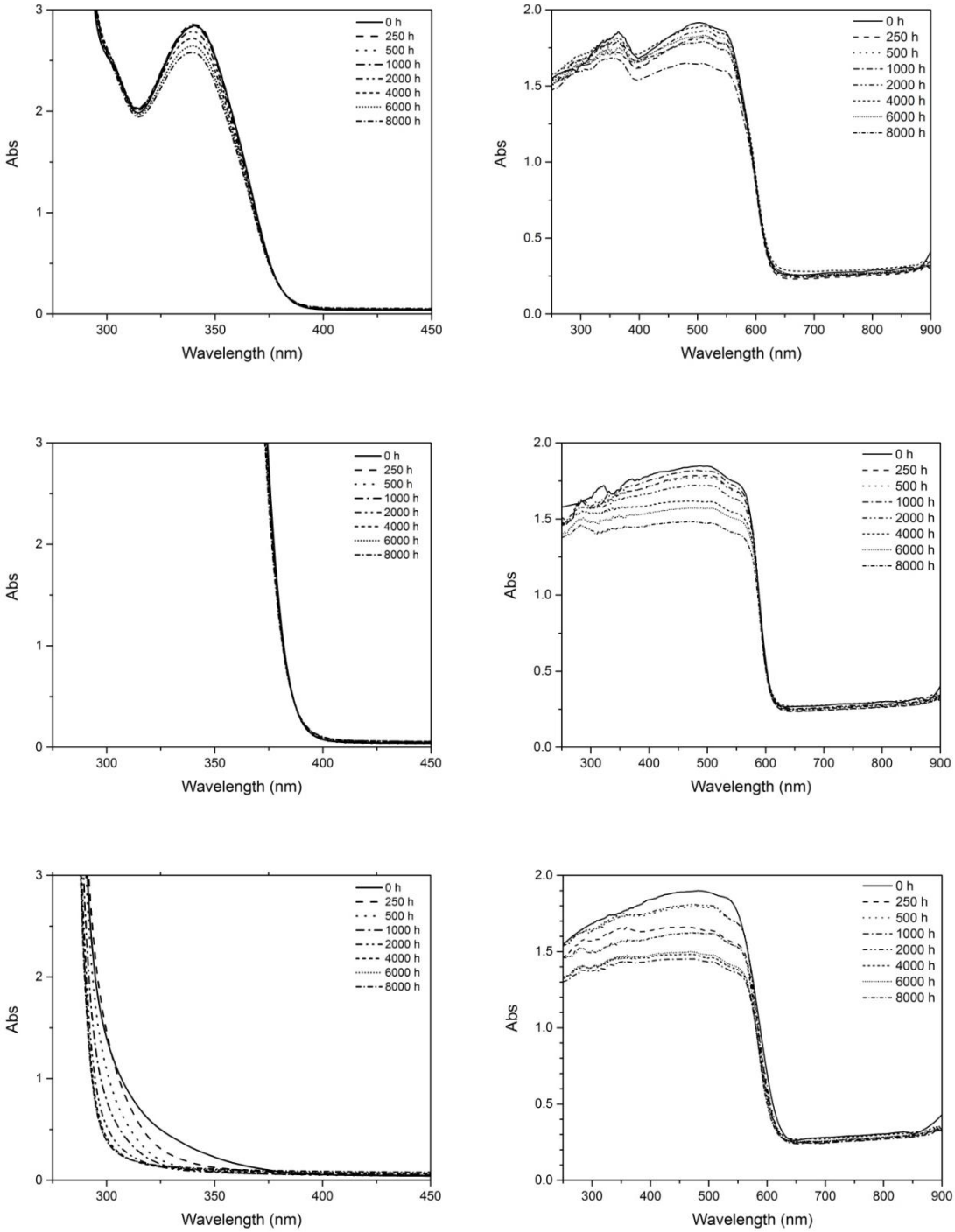


Figure A3.16: UV and UV-Vis absorbance spectra. On the left, from top to bottom, spectra of transparent samples, TPA, TPS, and TPL, acquired in transmittance mode. On the right, from top to bottom, spectra of red samples, RPA, RPS, RPL, acquired in reflectance mode.

Table A3.2: Colorimetry results from TPA, TPS, TPL, RPA, RPS and RAL samples during ageing

	0 h			500 h			1000 h			2000 h			4000 h			6000 h			8000 h		
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
TPA	91.32	-0.04	4.14	91.08	0.01	4.28	90.96	-0.03	4.53	90.80	0.01	4.38	90.67	-0.02	4.77	90.56	-0.07	5.15	90.07	-0.07	4.98
	±0.00	±0.01	±0.01	±0.06	±0.02	±0.04	±0.09	±0.02	±0.03	±0.01	±0.01	±0.01	±0.10	±0.02	±0.03	±0.04	±0.01	±0.04	±0.04	±0.01	±0.01
TPS	91.16	-0.25	4.78	90.90	-0.14	4.82	90.82	-0.18	5.04	90.61	-0.14	4.85	90.48	-0.16	5.20	90.30	-0.22	5.52	89.81	-0.21	5.37
	±0.12	±0.02	±0.03	±0.12	±0.02	±0.06	±0.10	±0.02	±0.02	±0.14	±0.01	±0.04	±0.04	±0.02	±0.02	±0.28	±0.02	±0.06	±0.17	±0.02	±0.03
TPL	89.75	-0.30	4.73	89.84	-0.22	5.09	89.79	-0.24	5.19	89.14	-0.15	4.81	88.99	-0.10	5.12	88.32	-0.10	5.52	87.26	-0.04	5.39
	±0.20	±0.01	±0.02	±0.13	±0.01	±0.04	±0.37	±0.02	±0.05	±0.23	±0.02	±0.02	±0.26	±0.02	±0.03	±0.22	±0.01	±0.05	±0.21	±0.02	±0.01
RPA	32.78	56.72	41.64	32.36	55.80	40.66	32.39	55.69	40.76	32.06	55.09	40.32	32.03	54.96	40.70	32.06	54.55	40.11	31.93	54.04	40.18
	±0.01	±0.01	±0.18	±0.00	±0.02	±0.10	±0.01	±0.02	±0.05	±0.02	±0.02	±0.09	±0.02	±0.03	±0.02	±0.04	±0.04	±0.19	±0.01	±0.03	±0.17
RPS	38.73	61.33	52.81	38.24	60.64	51.63	38.39	60.58	51.84	38.63	59.71	48.85	39.44	58.58	45.69	39.67	57.95	44.05	40.15	56.92	42.19
	±0.01	±0.02	±0.05	±0.01	±0.00	±0.04	±0.00	±0.01	±0.03	±0.01	±0.01	±0.07	±0.15	±0.14	±0.13	±0.12	±0.15	±0.14	±0.01	±0.02	±0.07
RAL	36.33	57.74	51.26	36.49	57.43	51.42	36.93	57.44	51.82	37.27	57.25	51.69	38.28	57.17	50.56	38.76	56.82	49.05	39.34	56.17	47.28
	±0.18	±0.25	±1.09	±0.06	±0.18	±0.87	±0.04	±0.19	±0.72	±0.10	±0.25	±0.91	±0.09	±0.27	±0.76	±0.04	±0.24	±0.51	±0.04	±0.13	±0.31

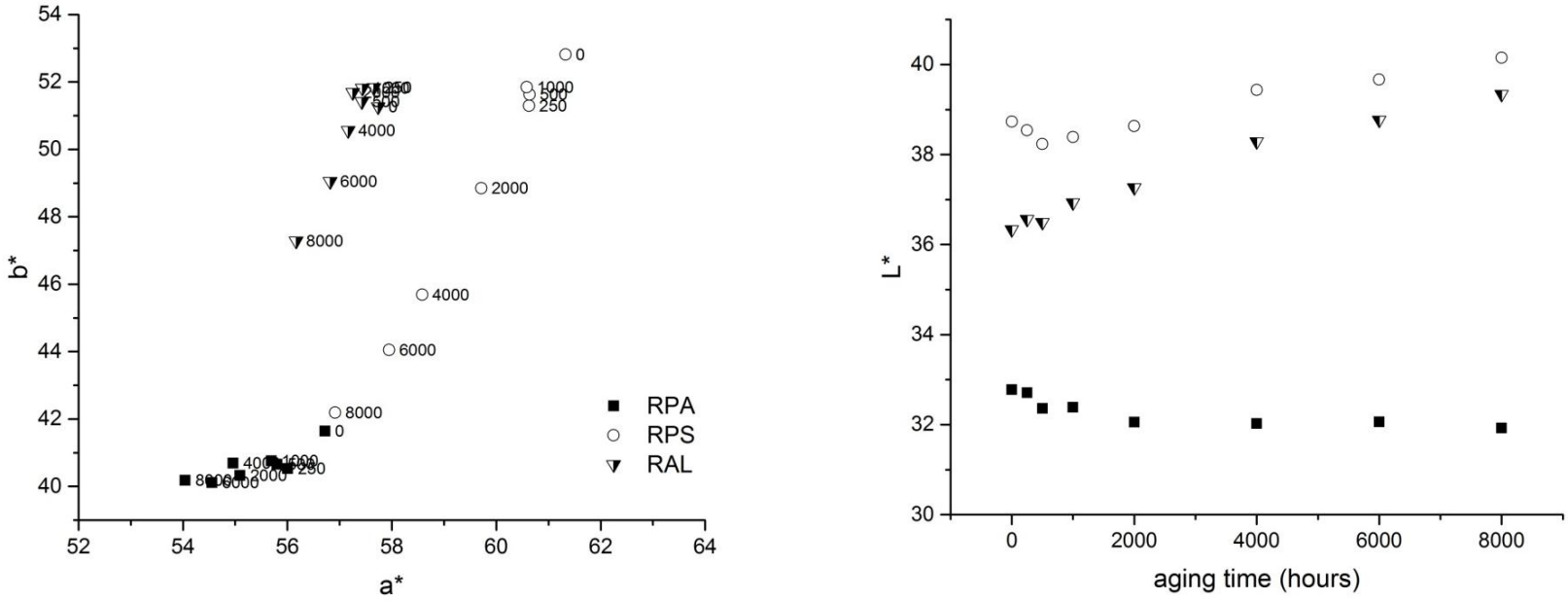


Figure A3.17: On the left, evolution of the a* and b* coordinates of the red PMMA samples along the artificial ageing. On the right, evolution of the L* coordinate.

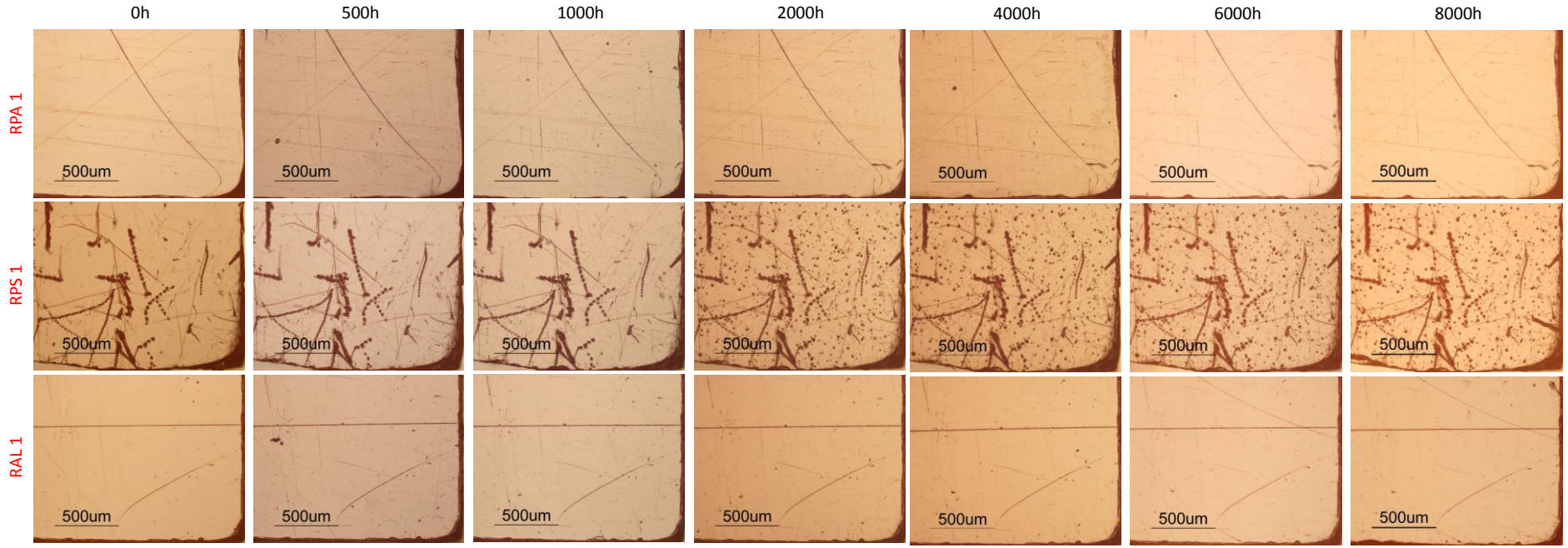


Figure A3.18: Microscopy images of the evolution of the PMMA surfaces of RPA, RPS and RAL samples during artificial ageing; aquired under reflected light and bright field mode.

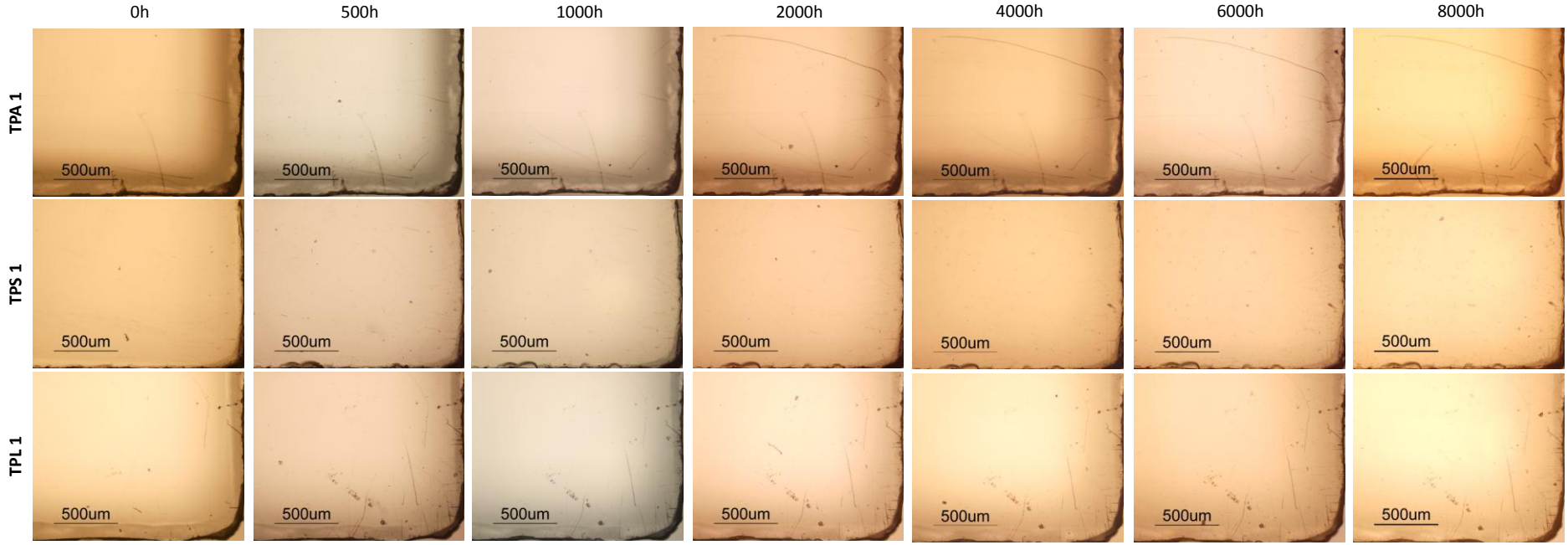


Figure A3.19: Microscopy images of the evolution of the PMMA surfaces of TPA, TPS and TPL samples during artificial ageing;

aquired under reflected light and bright field mode.

Table A3.3: Indentation results from TPA, TPS, TPL, RPA, RPS and RAL samples during ageing.

	0 h		250 h		500 h		1000 h		2000 h		4000 h		6000 h		8000 h	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
TPA	24.56	0.16	25.39	0.40	25.39	0.33	25.84	0.25	25.57	0.26	25.82	0.24	25.76	0.11	25.66	0.22
TPS	22.73	0.31	23.75	0.25	23.92	0.11	25.55	0.46	25.93	0.12	25.67	0.18	25.84	0.22	25.66	0.29
TPL	22.59	0.13	23.19	0.29	23.63	0.23	24.22	0.31	24.46	0.34	25.16	0.66	25.61	0.38	25.93	0.69
RPA	24.42	0.12			24.96	0.23			25.14	0.29	25.21	0.25	25.37	0.23	25.30	0.18
RPS	22.43	0.26			22.89	0.14			24.09	0.60	24.41	0.08	24.37	0.23	24.93	0.61
RAL	25.96	0.25			26.06	0.22			26.38	0.13	25.71	0.14	26.42	0.32	25.93	0.20

Appendix IV – Supplementary data to Chapter 6

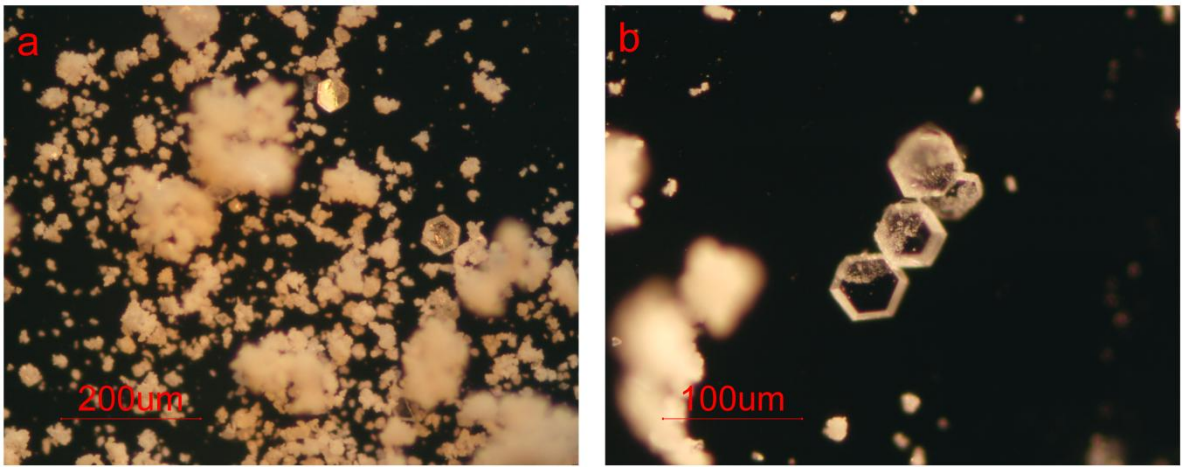


Figure A4.1: Microscopy images of synthetized crystals of plumbonacrite under reflected visible light in dark field (a-b).

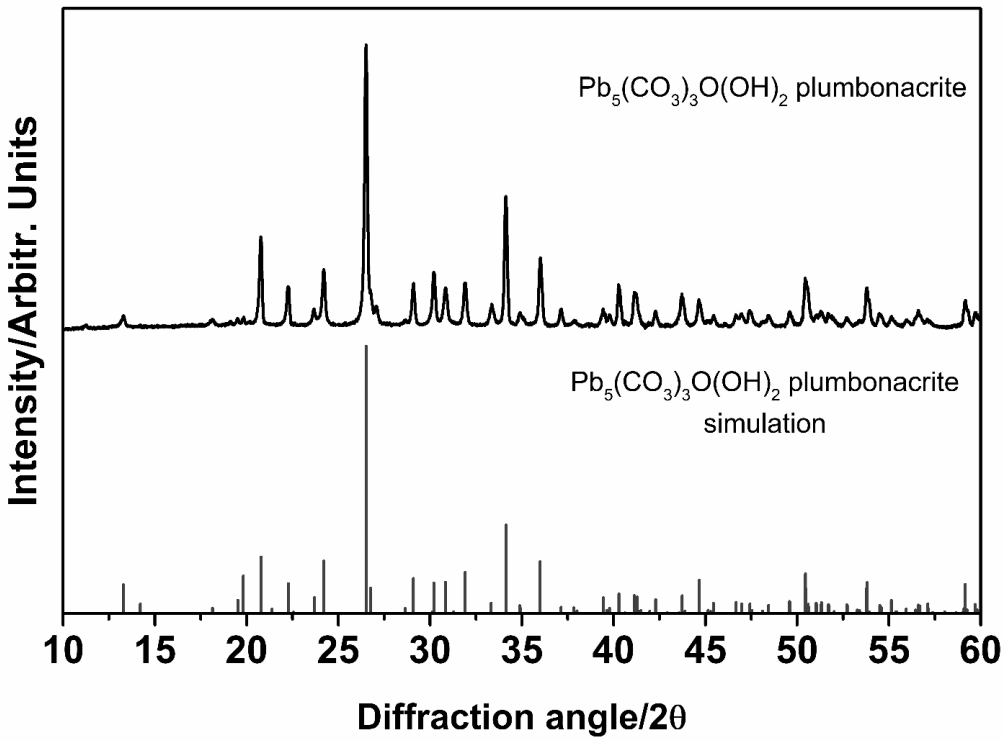


Figure A4.2: XRD patterns of the synthesizedplumbonacrite $Pb_5(CO_3)_3O(OH)_2$ and plumbonacrite $Pb_5(CO_3)_3O(OH)_2$ x-ray diffraction simulation with lattice parameters published in literature (primitive unit cells with a = 9.0921 Å, c = 24.923 Å).

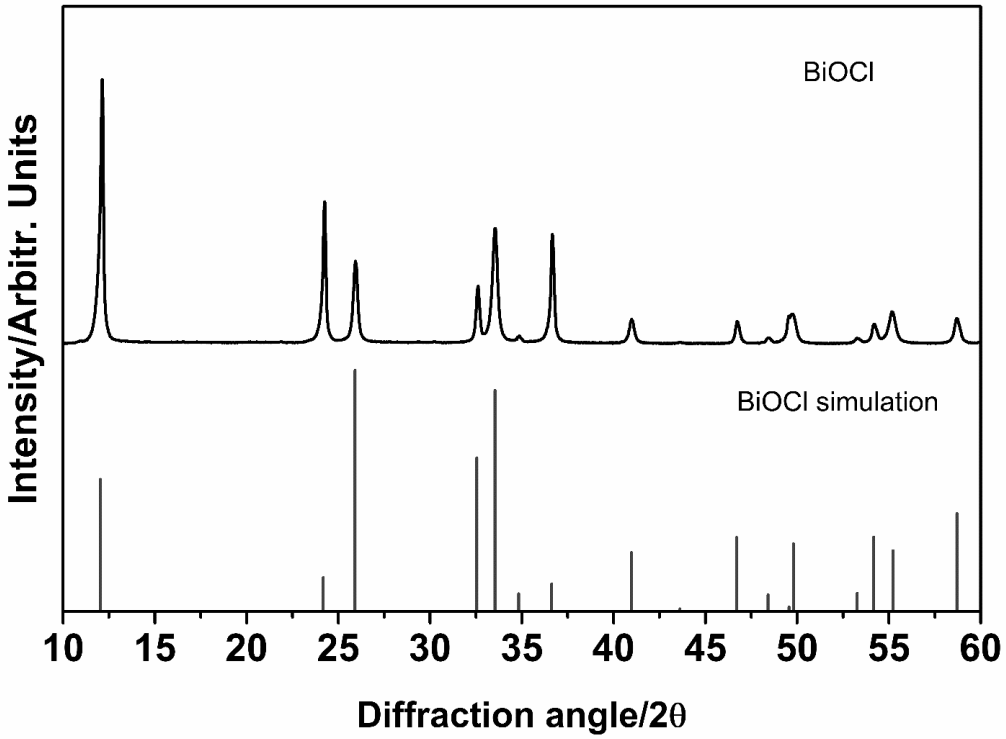


Figure A4.3: XRD patterns of synthesized bismuth oxychloride BiOCl and bismoclite BiOCl x-ray driffraction simulation with lattice parameters published in literature (primitive unit cells with a = 3.887Å, c = 7.354Å).

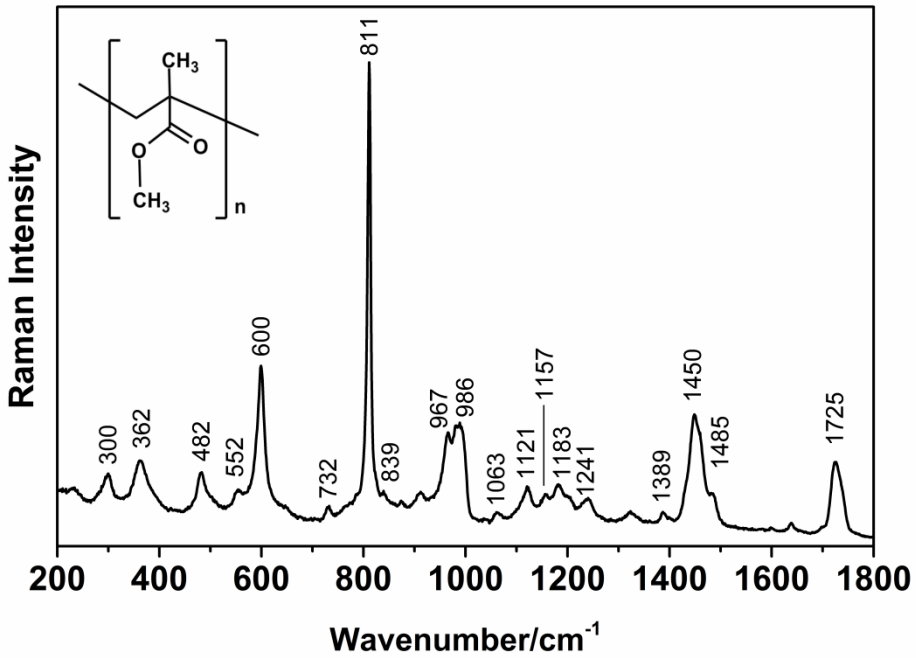


Figure A4.4: Vibrational spectrum of polymer PMMA collected in situ through Raman microscopy (632.8 nm excitation).

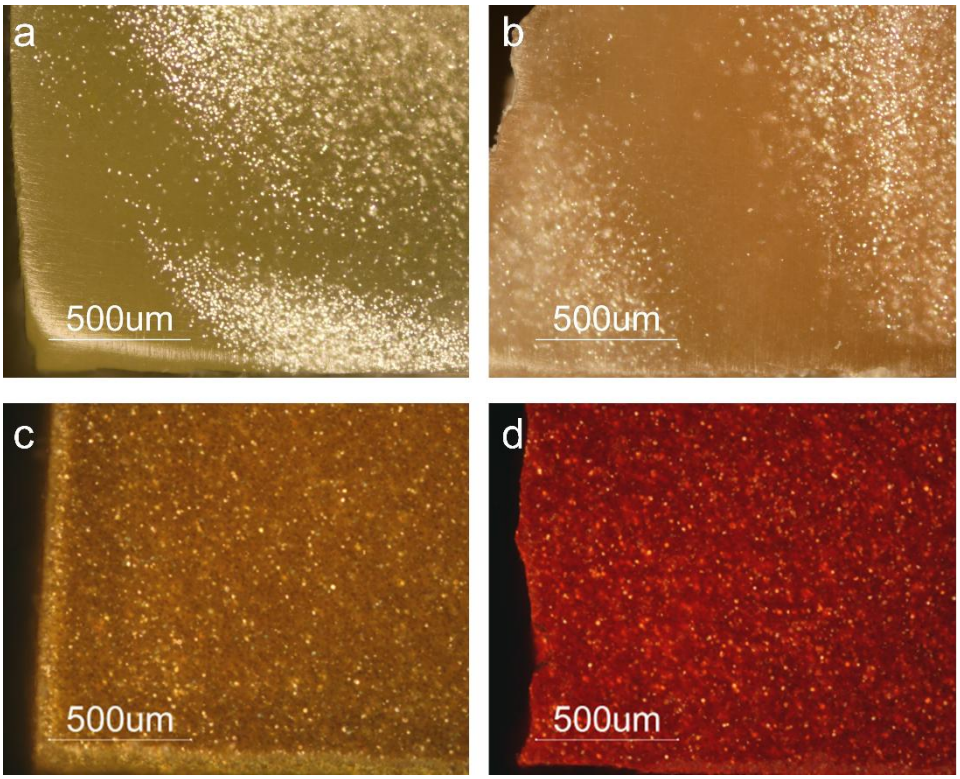


Figure A4.5: Microscopy images of the platelets in (a,c) yellow, (b) orange, (c) red pearlescent acrylic sheet probably made in 1960s (a-b) and 2000s (c-d) under reflected visible light in dark field.

Appendix V – Supplementary data to Chapter 7

Table A5.1: Gravimetry results of the surface treatment experiment.

	0 h (before)		0 h (after cleaning)		Δ (after-before)		2000 h		4000 h		Δ (4000 h - 0 h)	
	x̄ (g)	σ	x̄ (g)	σ	Δ	(%)	x̄ (g)	σ	x̄ (g)	σ	Δ	(%)
TPA– 1	5.76028	0.00036	5.75808	0.00023	-0.0022	-0.04	5.76406	0.00022	5.74569	0.00043	-0.0146	-0.25
TPA– 2	5.81821	0.00040	5.81582	0.00040	-0.0024	-0.04	5.82125	0.00020	5.80393	0.00033	-0.0143	-0.25
TPA– 3	5.77184	0.00033	5.76969	0.00029	-0.0022	-0.04	5.77579	0.00013	5.75938	0.00588	-0.0125	-0.22
TPA– 4	5.80612	0.00035	5.80361	0.00037	-0.0025	-0.04	5.80669	0.00013	5.78583	0.00033	-0.0203	-0.35
TPAU 1	4.63271	0.00023	4.62689	0.00014	-0.0058	-0.13	4.62893	0.00010	4.61695	0.00017	-0.0158	-0.34
TPAU 2	4.65932	0.00013	4.65324	0.00020	-0.0061	-0.13	4.65434	0.00011	4.64168	0.00019	-0.0176	-0.38
TPAU 3	4.68342	0.00024	4.67707	0.00023	-0.0064	-0.14	4.67790	0.00010	4.66492	0.00016	-0.0185	-0.40
TPAU 4	4.62654	0.00011	4.62028	0.00019	-0.0063	-0.14	4.61982	0.00012	4.60559	0.00019	-0.0209	-0.45
NW– 1	6.61610	0.00056	6.61440	0.00035	-0.0017	-0.03	6.58737	0.00011	6.54418	0.00032	-0.0719	-1.09
NW– 2	5.77202	0.00057	5.77060	0.00027	-0.0014	-0.02	5.74731	0.00012	5.70252	0.00026	-0.0695	-1.20
NW– 3	6.27745	0.00054	6.27467	0.00188	-0.0028	-0.04	6.25934	0.00013	6.21138	0.00028	-0.0661	-1.05
NW– 4	6.49671	0.00055	6.49472	0.00034	-0.0020	-0.03	6.47204	0.00010	6.42785	0.00027	-0.0689	-1.06
NWU1	5.07314	0.00029	5.06424	0.00021	-0.0089	-0.18	5.05201	0.00006	5.02123	0.00022	-0.0519	-1.02
NWU2	4.50240	0.00025	4.49368	0.00019	-0.0087	-0.19	4.48270	0.00007	4.45252	0.00020	-0.0499	-1.11
NWU3	4.97589	0.00025	4.96709	0.00019	-0.0088	-0.18	4.95470	0.00009	4.92367	0.00019	-0.0522	-1.05
NWU4	5.08357	0.00024	5.07444	0.00017	-0.0091	-0.18	5.05986	0.00008	5.02850	0.00016	-0.0551	-1.08

Table A5.2: Vickers hardness results of the surface treatment experiment.

	0 h		4000 h	
	x̄	σ	x̄	σ
TPA ref	24.6	0.2	24.6	0.3
TPA– 1			24.7	0.1
TPA– 2			24.7	0.2
TPA– 3			24.6	0.2
TPA– 4			25.0	0.3
NW ref	22.8	0.7	26.1	0.7
NW– 1			26.9	0.5
NW– 2			26.3	0.3
NW– 3			26.2	0.3
NW– 4			26.8	0.5

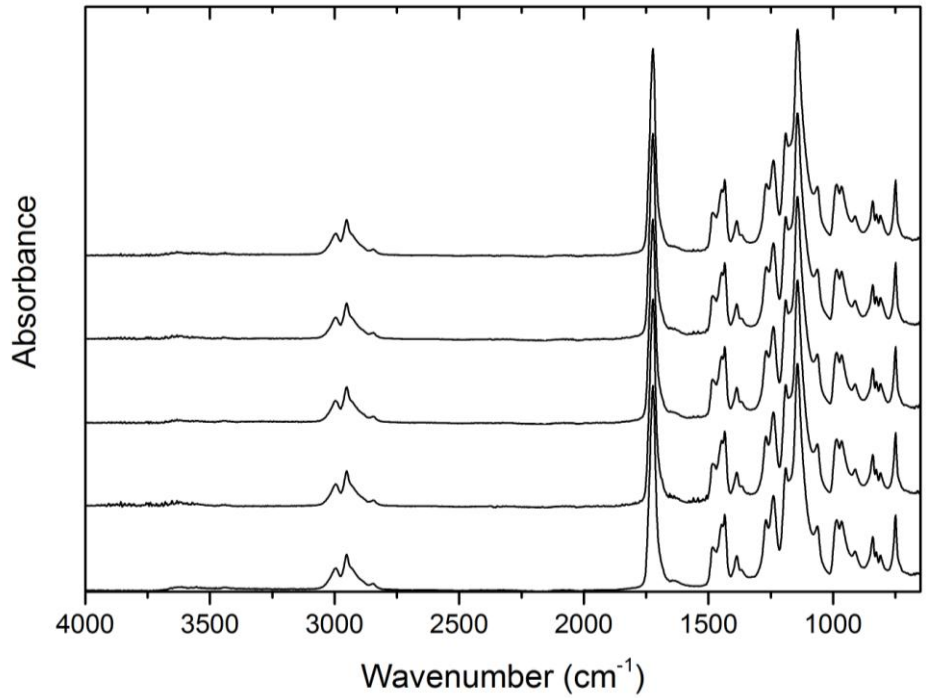


Figure A5.1: Infrared spectra of TPA plane samples. From bottom to top: reference sample 0 h; samples with treatment 1, 2, 3 and 4 after 4000 h of artificial ageing.

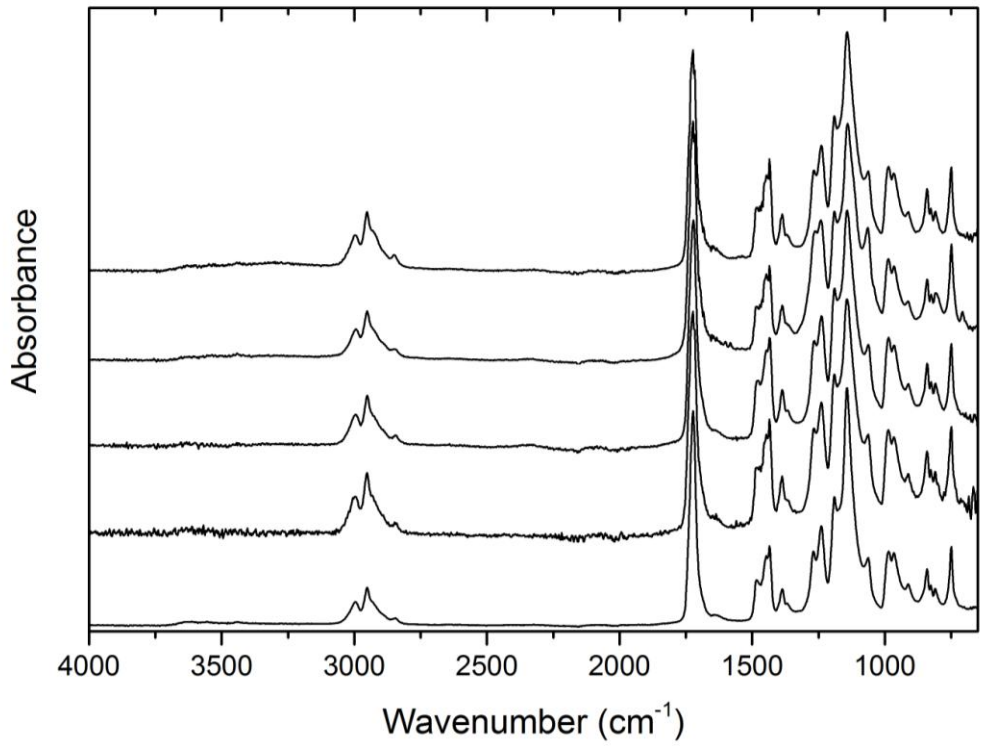


Figure A5.2: Infrared spectra of TPA curved samples. From bottom to top: reference sample 0 h; samples with treatment 1, 2, 3 and 4 after 4000 h of artificial ageing.

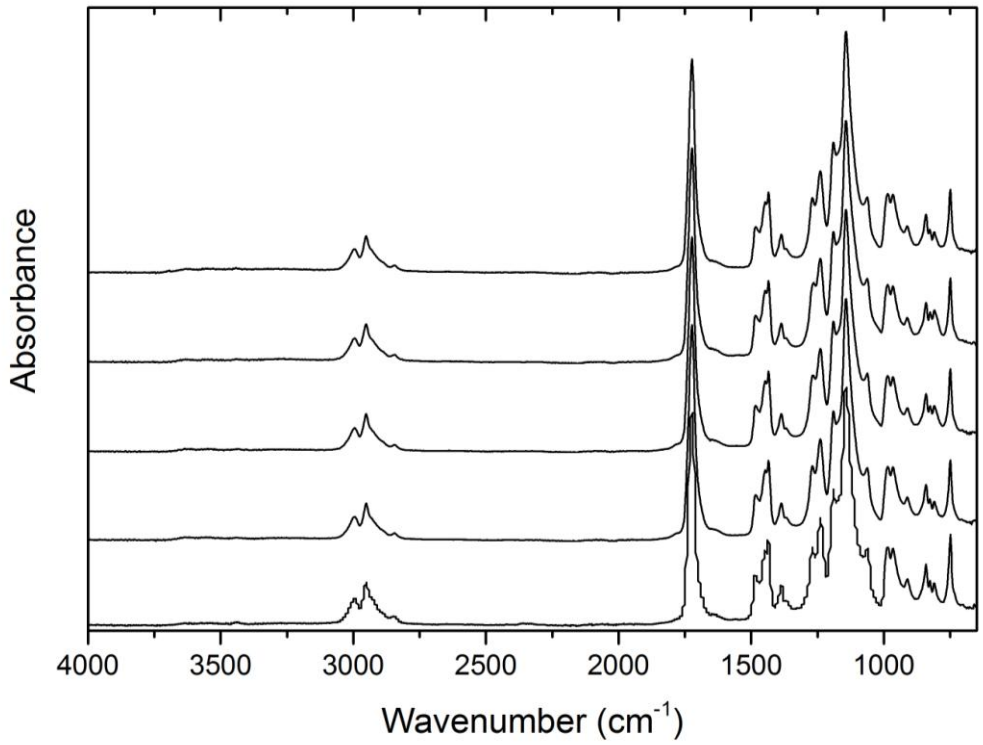


Figure A5.3: Infrared spectra of NW plane samples. From bottom to top: reference sample 0 h; samples with treatment 1, 2, 3 and 4 after 4000 h of artificial ageing.

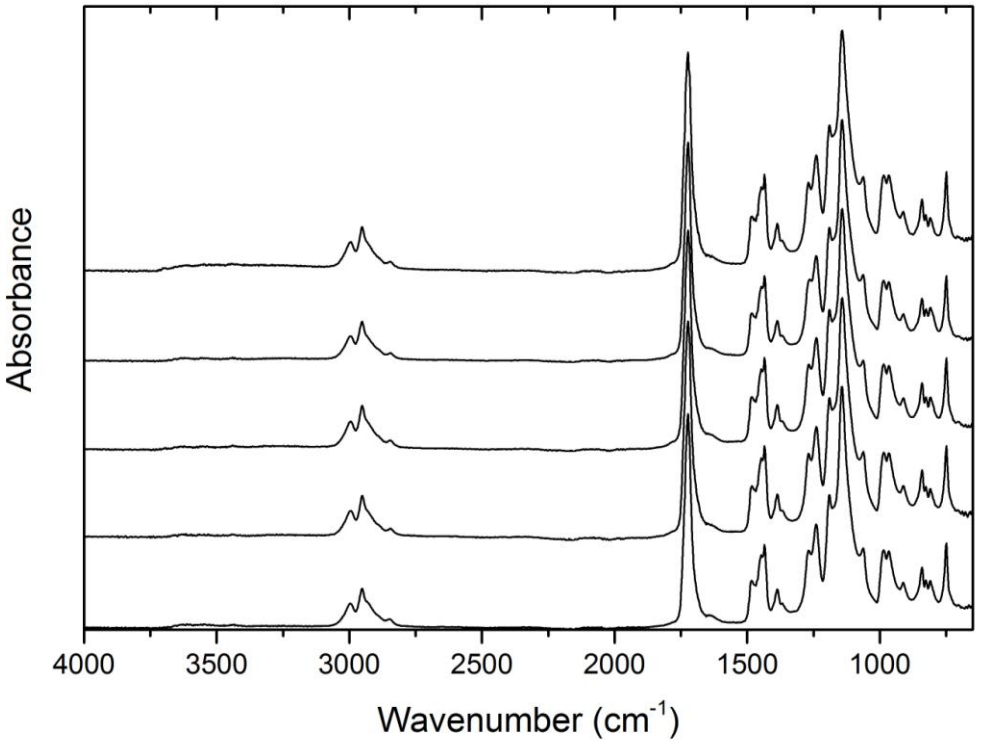


Figure A5.4: Infrared spectra of NW curved samples. From bottom to top: reference sample 0 h; samples with treatment 1, 2, 3 and 4 after 4000 h of artificial ageing.

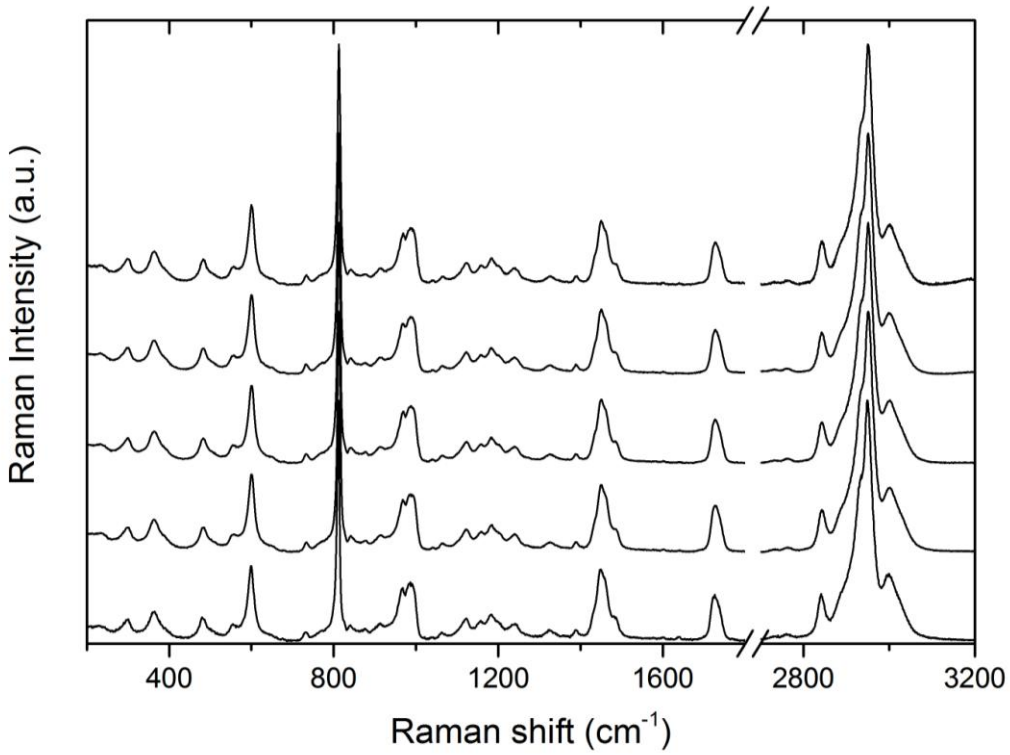


Figure A5.5: Raman spectra of TPA plane samples. From bottom to top: reference sample 0 h; samples with treatment 1, 2, 3 and 4 after 4000 h of artificial ageing.

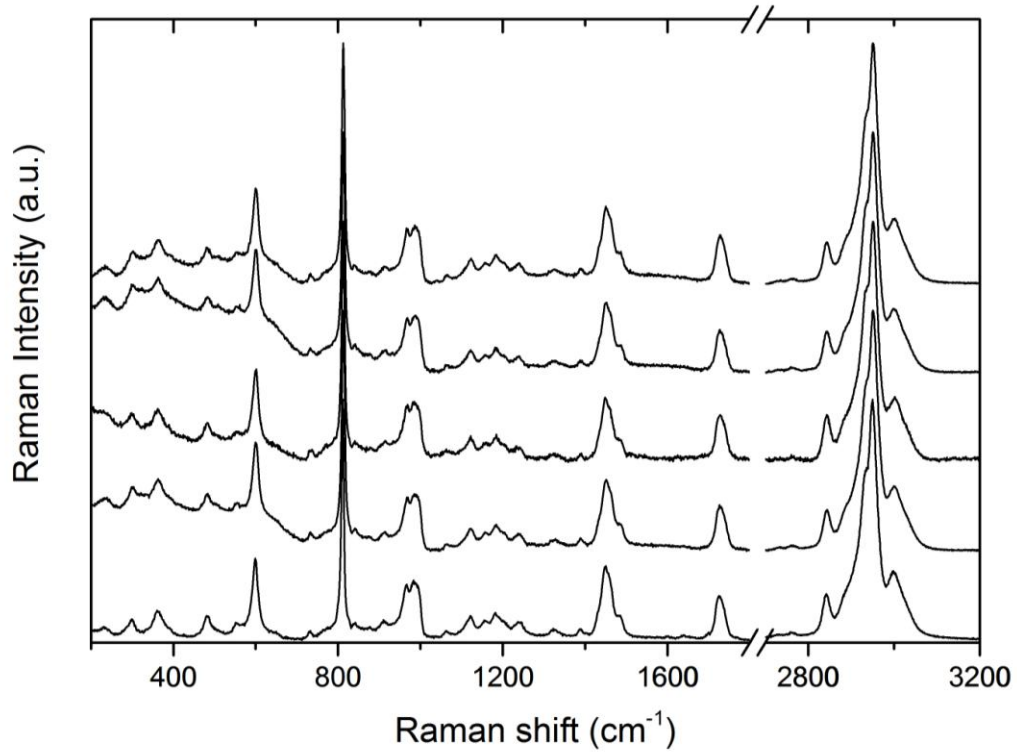


Figure A5.6: Raman spectra of NW plane samples. From bottom to top: reference sample 0 h; samples with treatment 1, 2, 3 and 4 after 4000 h of artificial ageing. Table A5.3: Colorimetry results of the surface treatment experiment.

	0 h (before)			0 h (after cleaning)			2000 h			4000 h			Δ			
	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	ΔL*	Δa*	Δb*	**ΔE**
TPA– 1	87.79	-0.05	4.39	88.81	-0.02	4.18	90.21	0.00	4.43	89.85	-0.13	5.06	2.06	-0.08	0.67	**2.16**
	±0.81	±0.04	±0.10	±0.19	±0.03	±0.07	±0.17	±0.04	±0.05	±0.19	±0.05	±0.06				
TPA– 2	88.37	0.00	4.36	88.94	-0.04	4.07	90.30	-0.03	4.31	90.00	-0.13	4.94	1.63	-0.12	0.58	**1.73**
	±0.05	±0.09	±0.02	±0.26	±0.00	±0.06	±0.10	±0.04	±0.10	±0.31	±0.04	±0.07				
TPA– 3	88.48	-0.06	4.07	89.07	-0.02	4.10	90.36	-0.03	4.40	89.98	-0.19	5.25	1.50	-0.13	1.18	**1.92**
	±0.39	±0.04	±0.06	±0.07	±0.02	±0.10	±0.15	±0.03	±0.17	±0.15	±0.05	±0.13				
TPA– 4	88.71	-0.03	4.15	88.46	-0.03	4.16	90.06	0.01	4.51	89.71	-0.11	5.10	1.00	-0.08	0.95	**1.38**
	±0.21	±0.02	±0.11	±0.40	±0.03	±0.09	±0.03	±0.03	±0.09	±0.14	±0.04	±0.13				
NW– 1	72.44	-0.14	9.86	72.38	-0.23	9.83	30.85	0.08	0.20	34.82	0.07	-1.04	-37.62	0.21	-10.90	**39.16**
	±1.03	±0.30	±0.29	±0.90	±0.14	±0.32	±0.91	±0.09	±0.60	±7.10	±0.09	±0.27				
NW– 2	73.68	-0.11	9.50	73.74	-0.11	9.60	33.21	0.24	0.87	36.83	0.05	-0.81	-36.85	0.16	-10.32	**38.27**
	±0.97	±0.16	±0.25	±1.11	±0.12	±0.36	±0.97	±0.06	±0.23	±9.62	±0.07	±0.09				
NW– 3	73.53	-0.25	9.83	73.70	-0.26	9.71	35.59	0.42	0.56	31.52	0.11	-1.32	-42.01	0.36	-11.15	**43.46**
	±1.03	±0.09	±0.35	±1.03	±0.10	±0.26	±1.17	±0.05	±0.40	±3.31	±0.12	±0.27				
NW– 4	70.92	-0.16	10.16	70.55	-0.07	10.07	35.31	0.14	0.41	30.51	0.14	-1.71	-40.41	0.30	-11.87	**42.11**
	±1.86	±0.15	±0.30	±2.12	±0.17	±0.18	±1.98	±0.15	±0.58	±1.13	±0.05	±0.17				

The mountain is supported on a "base" that we have already stressed…
And perhaps on others that remain to be discovered.
It is done, it isn't finished.
It is a good sign.

(Manuel Zimbro, 2001, about *Montanha de flores* [Mountain of flowers] by Lourdes Castro, In Fernandes and Zimbro 2003, 132)